

Silicon and Carbon Substrates Induced Arrangement Changes in Poly(styrene-*b*-isoprene-*b*-styrene) Block Copolymer Thin Films

Iñaki Zalakain, Jose Angel Ramos, Raquel Fernandez, Haritz Etxeberria, Iñaki Mondragon

'Materials + Technologies' Group, Dpto Ingeniería Química y M Ambiente, Escuela Politécnica, Universidad País Vasco/Euskal Herriko Unibertsitatea, 20018 Donostia-San Sebastián, Spain

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ABSTRACT: Poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer ordering in thin films was studied using two selective substrates as carbon and silicon. Atomic force microscopy (AFM) and contact angle measurements were employed to examine the affinities between domains and surrounding interfaces. The surface morphology was examined by AFM using different amplitude ratios. Results showed polyisoprene (PI) domain layer formation in the outermost film layer. On the other hand, the layer close to substrate adopted different arrangements on silicon and carbon substrates. Topographical and phase images revealed that in both substrates with the thickest films, the interactions between substrate and block

domains were not enough to induce surface ordering being the morphology independent of employed substrate. However, decreasing film thickness, SIS thin films displayed a variety of arrangements such as perforated lamellae and cylindrical morphologies. Depending on substrate, these morphologies were achieved in different film thicknesses. Finally, the thinnest film did not adjust to characteristic domain spacing commensurability and terraces formation was observed. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1552–1558, 2012

Key words: block copolymer; thin films; substrate; thickness; atomic force microscopy

INTRODUCTION

Block copolymers consisting of two or more homogeneous polymer chains chemically linked by covalent bonds can self-assemble into a variety of morphologies as lamellar, hexagonally packed cylindrical, body centered cubic spherical, gyroidal, and hexagonally perforated layers, among others.^{1–7} The microphase separation capability of block copolymers turns into an easy method to produce templates with features in the range of 10–100 nm.^{1,2,4–7} In particular, block copolymer thin films are suitable for applications that require minimum film thickness. Leibler developed the theory of microphase separation in diblock copolymers analyzing the necessary conditions for the different or-

dered nanostructures formation.³ Leibler theory is based on the theory of Flory–Huggins of phase segregation. In bulk, the most relevant parameters of this theory are χN (χ is the Flory parameter referring interactions between blocks; N is the polymerization index), and f , volume fraction of the constituent blocks. High χN values produce microphase segregation due to repulsion between blocks. In thin films, some extra parameters affect phase segregation. Interfacial interactions with the boundary surface play an important role in block copolymer thin films. Due to the effect of interfacial interactions, block copolymer thin films can show different morphologies respect to the bulk. Generally, in thin films the copolymer domains with lower surface tension tend to be located in the outermost layer to minimize surface energy.^{5,7} In the case of the layer close to the substrate, if one domain of the block copolymer has a strong affinity with the substrate, this domain orients parallel to this surface.⁷ The thickness is other important parameter in thin films. Thickness (t) is commensurate with characteristic domain spacing (C).^{5,8} If the same domains are located at both interfaces, outermost layer of the film surface and substrate, block copolymer has symmetric wettability.⁷ In this case, the thickness keeps the relationship $t = nC$ (where n is an integer number). On the other hand, if both domains present similar affinity

Correspondence to: I. Mondragon (inaki.mondragon@ehu.es).

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with the substrate, both domains can be located in the substrate, but if they have different surface tensions one of the block domains can be located in the outermost layer, and thus block copolymer has an asymmetric wettability. In this case, the thickness keeps the relationship $t = (n + 1/2)C$. Nevertheless, the film shows an inhomogeneous surface where the film thickness is not adjusted to characteristic domain spacing commensurability ($t \neq nC$)^{5,6,8,9} showing terraces formation (macroscopic areas of different thicknesses). These areas with different thicknesses tend to maintain domain period commensurability. Thus, terrace formation shows a step height of $t = nC$ with stable morphologies.^{8,10,11}

Symmetric diblock copolymer thin films have been studied over the past decades.^{4,7,12–14} In those systems, the most common morphology is lamellar. If one block preferentially wets any interface (polymer–substrate or polymer–air interfaces) the lamellae will orient parallelly to the interface. On the contrary, if both domains have similar affinities with the substrate or similar surface tension, lamellae will orient perpendicularly to the interface.^{7,13} But in most of cases, symmetric copolymer thin films do not show a different morphology of the lamellar. These systems only suffer a reorientation of lamellae depending on surrounding environment.^{7,13} However, asymmetric diblock copolymers with strong boundary interactions can show different morphologies respect to bulk state such as substrate parallel or perpendicular cylinders, on perforated lamellae. Results on morphological variations of thin asymmetric block copolymers films due to differences in film thicknesses and/or to interactions between substrate and domains have been shown.^{5,11,15,16} Most researches with asymmetric block copolymer thin films are for a specific copolymer composition, type of substrates, or annealing conditions. Unfortunately, there are still not general conclusions for all kind of asymmetric systems and each system shows a particular behavior.^{5–7,11} The present work is based on Krausch and coworkers work.⁵ They examined poly(styrene-*b*-butadiene-*b*-styrene) (SBS) copolymer behavior in different substrates observing variations in the morphologies depending on the employed substrate. In this work, the behavior of asymmetric poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer was examined using two different substrates with different polarities to analyze block domains selectivity. Outermost and inner layers composition of SIS films were studied by atomic force microscopy (AFM) applying different tip-sample forces. On the other hand, the composition in the layer near to the substrate was analyzed by contact angle (CA) measurements for silicon wafer and highly oriented pyrolytic graphite (HOPG) substrate. Mathematical approaches were used to calculate number of

cylinders layers in a film, cylinders diameter, and topmost layer thickness. Film nanostructuring behavior was also examined for different film thicknesses to analyze the substrate influence in the obtained surface morphologies.

EXPERIMENTAL SECTION

Sample preparation

In this work, SIS triblock thin films were obtained using toluene solutions with different concentrations from 1.0 to 4.0 wt %. Two different substrates were employed: silicon wafer and freshly cleaved HOPG. SIS from Kraton Polymer with molecular weights $M_{w,PS} = 17,460 \text{ g mol}^{-1}$ and $M_{w,PI} = 40,740 \text{ g mol}^{-1}$ (polystyrene—PS, polyisoprene—PI) with a PS weight fraction of $\Phi_{PS} = 0.3$ was used. Polyisoprene ($M_w \approx 40,000 \text{ g mol}^{-1}$) and polystyrene ($M_w \approx 80,000 \text{ g mol}^{-1}$) were purchased from Aldrich and Basf, respectively. PS and PI homopolymer films (in 20 wt % SIS/toluene solution) were prepared on glass slides using dip-coating technique. These films were subsequently used as substrates to carry out CA measurements. Block copolymer films were also prepared by dip-coating. Prior to thin film preparation on silicon wafer, the substrate was cleaned to remove organic residues. The wafer was rinsed in dichloromethane in an ultrasonic bath for 15 min at 30°C and afterward in a mixture of water, ammonia solution (25%), and hydrogen peroxide (30%) with a volume ratio 6 : 1 : 1 for 25 min at 80°C. The silicon wafer was rinsed several times with pure water (Millipore) and dried with a nitrogen flow. Freshly cleaved HOPG substrate was prepared by pressing sticky tape against the top HOPG surface and then peeling off the tape.

The preparation of block copolymer thin films was carried out by the following procedure. The silicon wafer and freshly cleaved HOPG substrates were dipped into SIS/toluene solutions with a rate of 40 mm/min, and subsequently pulled out from the solution with a rate of 5 mm/min, thereafter being exposed to air for drying.¹⁷ The used SIS copolymer self-assembled at room temperature conditions.^{18,19}

Atomic force microscopy

SIS thin films morphological features were investigated using AFM (Nanoscope IV, Dimension 3100—Veeco). Topographic and phase images were obtained in tapping mode under room conditions with typical rate of $\sim 1 \text{ line} \times \text{s}^{-1}$ with a resonance frequency of $\sim 300 \text{ kHz}$. Measurements were performed with 512 scan lines. Several regions were scanned obtaining similar images. AFM images analysis was carried out with WSxM software (Nanotech

Electronica). Analysis was performed in tapping-mode at different tip-sample force levels. Morphological features were examined using minimal forces to analyze the outermost layer of the film, or using appropriate forces to check dipper layers.^{6,20,21} These measurements were carried out with an imaging aspect ratio of 1 : 4 to minimize the signal distortion in the scan slow direction due to thermal drift.^{5,16} For measuring film thickness, scan size was 20–30 μm and an imaging aspect ratio of 1 : 4 was used. Films were scratched with a brass wire before recording topographic images. Film thickness was measured by means of height differences from the film to a bare substrate using the software analysis.

Contact angle

Static CAs of PS, PI, HOPG, and silicon wafer substrates were measured to study the affinity between the different copolymer components and the substrates. Thus, PS and PI domains possible arrangements in different substrates were analyzed. Measurements were carried out at room temperature with a Dataphysics OCA20s instrument, employing deionized water as wetting liquid and a drop volume of 2 μL . Measurements were carried out after 30 s period of time to ensure the equilibrium state. At least five measurements were performed in every sample obtaining similar results.

RESULTS AND DISCUSSION

Thin film arrangements

Understanding block copolymer behavior is important to obtain specific morphologies for certain applications. In the case of block copolymer thin films, the knowledge of both the boundary interactions and the influence of film thickness is required. To deepen on this knowledge, first, the influence of substrate in the resulting copolymer morphology has been analyzed using substrates with affinities to one of the blocks or to both of them. Furthermore, the thickness influence in the resultant morphology has also been analyzed.

In a block copolymer in contact with air, the domains with lower surface tension locate on the film outermost layer. In the case of SIS, surface tension for PS and PI domains are 39.5 mN m^{-1} and 32.5 mN m^{-1} , respectively. Considering these values, PI block should be located on the film outermost layer. AFM characterization was used to examine the outermost and the inner layers compositions in the block copolymer films applying several tip-sample forces.^{6,20,21} For these measurements, the used film was thick to avoid substrate influence. In the case of a soft outermost layer, the topography can be imaged

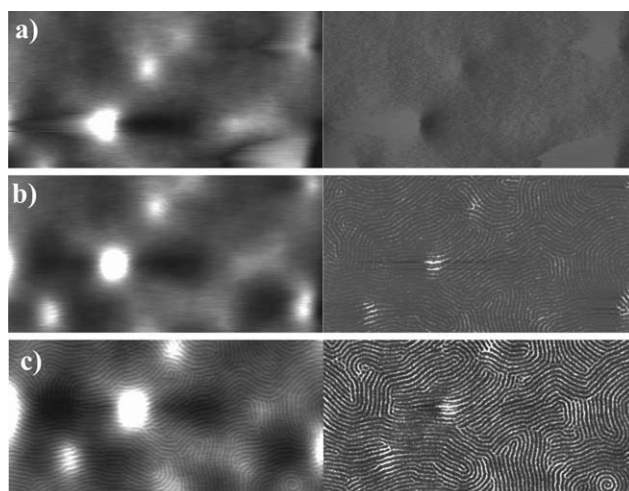


Figure 1 Topographical (right) and phase (left) images taken from the same area using different amplitude ratios: (a) 0.985, (b) 0.957, (c) 0.886. Scan size 3 μm \times 1.5 μm .

by applying a minimum tip-sample force not enough to penetrate the copolymer surface. Increasing tip-sample forces, the tip penetrates the outermost layer. Thus, using higher forces the domains under the outermost layer can be detected. Tip-sample forces are referred to the amplitude ratio, r_{sp} , defined by the quotient between amplitude set-point used for the feedback control, A_{sp} , and amplitude set-point value in the proximity of the sample surface, A_0 , $r_{\text{sp}} = A_{\text{sp}}/A_0$. Three different r_{sp} values, $r_{\text{sp}} = 0.985$, 0.957, and 0.915 were used to examine film topographical characteristics. In Figure 1(a–c), three different images with different tip-sample forces are shown. For the maximum amplitude ratio ($r_{\text{sp}} = 0.985$) applied, corresponding with the lowest force, the absence of any pronounced features in both height and phase images suggest that the thin film outermost layer was a homogeneous layer. Decreasing amplitude ratio, the upper part of self-assembled domains was visualized for $r_{\text{sp}} = 0.957$ and 0.915 amplitude ratios. The smallest amplitude ratio value allowed to clearly observing cylindrical domain features underneath of the top layer. Taking into account the copolymer domain volumetric fractions, PS and PI surface tensions and AFM analysis results, the following facts are envisaged: first, the outermost layer consisted mainly of polyisoprene and second, the film inner region was composed of polystyrene cylindrical domains embedded in PI matrix.

On the other hand, water CA measurements were used to analyze affinities between the chains of block copolymer and substrates. CAs values were 99°, 72°, <10°, and 86° for PS layer, PI layer, silicon wafer, and HOPG, respectively, similar to those reported by other authors.^{22–25} In the case of HOPG, the proximity of PS and PI CA values with carbon substrate CA suggest that both domains can wet the

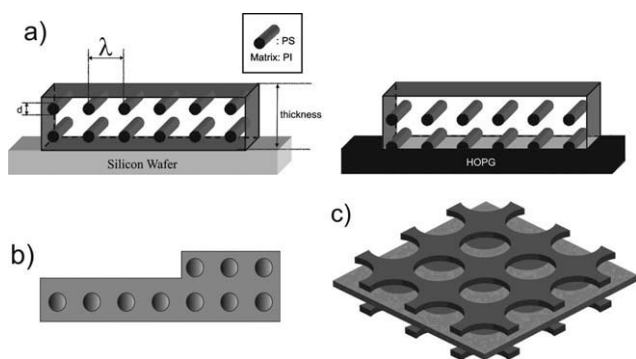


Figure 2 Arrangements of poly(styrene-*b*-isoprene-*b*-styrene) films: (a) left, on silicon; right, on carbon substrate; (b) Terrace formation; (c) Perforated lamellae.

carbon substrate. Otherwise, taking into account silicon wafer CA, this substrate should be more selective for PI block. Considering block copolymer domains interfacial interactions with the silicon and carbon substrate and the outermost surface layer composition, two possible SIS thin film arrangements could occur depending on the type of substrate [Fig. 2(a)]. In silicon wafer, considering PI location in both interfaces, the wettability should be more or less symmetric. Thus, as above mentioned, the film thickness will keep $t = nC$ relationship. However, in carbon substrate, PI and PS blocks should wet the substrate, whereas only PI block would form the outermost layer. Hence the wettability should be asymmetric, the thickness obeying the relationship $t = (n + 1/2)C$. These facts are discussed here below also taking into account film thickness.

Thickness influence in thin film morphologies

Another goal of the work was the analysis of the morphological features of the block copolymer thin films as a function of their thickness. Depending on the substrate, differences in block copolymer morphologies could be observed by varying the thickness. Figure 2 shows different copolymer arrangements such as cylindrical morphologies, terrace formation, and perforated lamellae depending on the film thickness.

SIS films in silicon wafer substrates

As above mentioned, the SIS copolymer in silicon wafer substrate should have a symmetric wettability where PI domains would be located in both air and substrate interfaces. The average cylinder-to-cylinder distance (λ) obtained for a SIS thick film from an AFM image (not shown in the present work) was 30 nm. The characteristic domain spacing is given by $C = \lambda \cos 30$. Taking into account λ distance and considering PS cylinders were hexagonally distributed,

the thickness between layers keeps the relationship of $t = n\lambda \cos 30$. The calculated distance between layers is 26 nm. Theoretical approach was used to obtain PS cylinders diameter (d). This can be estimated from $d = 2(3^{1/2}f/2\pi)^{1/2}\lambda$ where f is the volume fraction of minority block.^{8,26} Taking into account PS volume fraction 0.29, PS cylinder diameter should be 17 nm. On the other hand, the thickness of PI topmost layer can be estimated considering the same PI amount on each side of PS cylinders. The PI topmost layer can be estimated as 8–9 nm, it means the half of the difference between λ and cylinders diameter.

Figure 3(a–d) shows different surface morphologies of SIS films on silicon substrates as a function of their thickness. Film thickness variations were achieved by varying employed SIS/toluene solution concentration. For very thin films a heterogeneous surface with terraces formation was seen, as shown in Figure 3(a). The surface exhibited two regions with different thicknesses. The dominant morphology in S_1 region (7–10 nm) was composed by randomly distributed PS short cylinders onto PI matrix. Due to the low film thickness in this region, the domains could not have enough mobility to get a perfect arrangement. However, in S_2 region which has 28–30 nm thickness, the surface exhibited PS cylinders parallelly oriented to the substrate into the PI matrix. On the other hand, for slightly higher thickness [Fig. 3(b)], the film also showed two different regions. In the S_3 region (30–32 nm), the surface displayed a single layer of PS cylinders parallelly oriented to the substrate but most of the surface (S_4 region with 24–26 nm) was covered by a perforated lamellae morphology where PS matrix was perforated by perpendicular PI cylinders. The outermost and substrate close layers were composed by PI domains and consequently, the layer below the surface would have PI volume fraction depletion becoming the PS the majority component. This composition variation would induce a phase inversion from PS cylinders crossing the PI matrix to PI cylinders crossing PS matrix.^{5,27} The thickest film surface with 54–57 nm [Fig. 3(c)] displayed a homogeneous topography composed by two layers of PS cylinders parallel to the substrate embedded in the PI matrix. Increasing the film thickness, the copolymer showed similar morphologies (not shown in the present work) because the substrate/block copolymer interactions were not enough to influence the surface arrangement. Therefore, cylinders aligned parallel to the substrate can be considered the predominant morphology in bulk for this copolymer. The assumption of SIS conformation in silicon substrate can be considered appropriate considering that measured film thicknesses obey the theoretical approach above proposed for symmetric system.

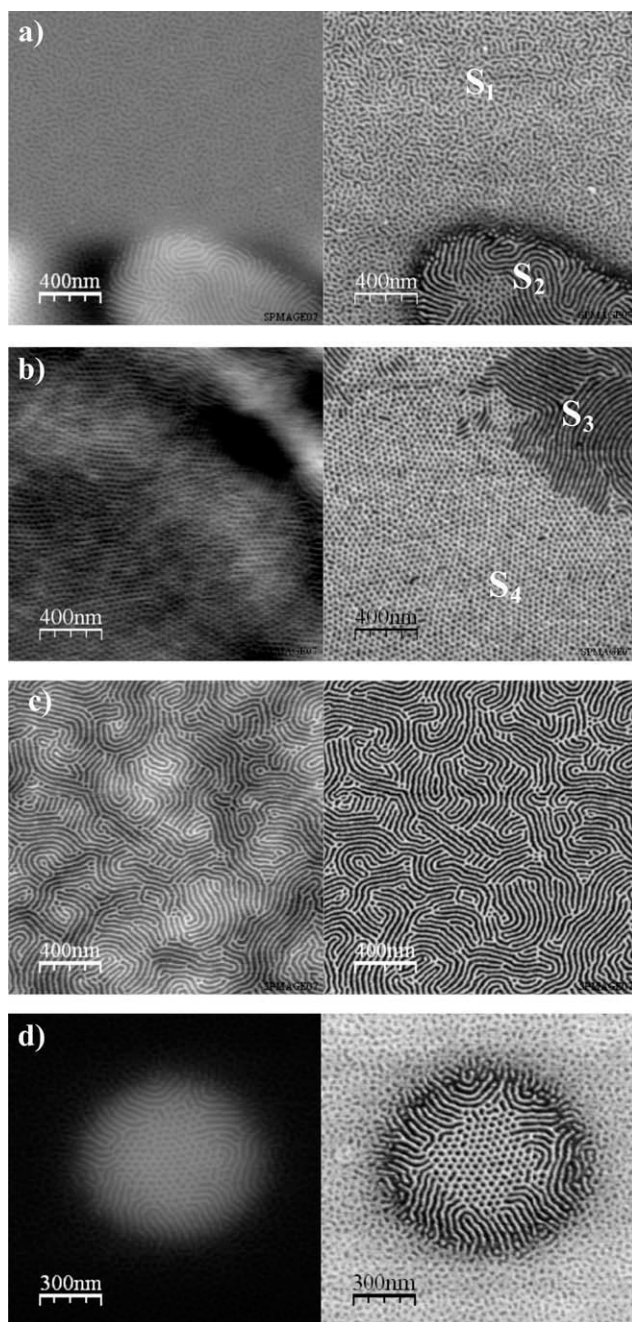


Figure 3 AFM height (left) and phase (right) images of films obtained from SIS/toluene solutions with different concentrations on silicon wafer substrate. Films show regions with different thicknesses: (a) 1.0 wt % SIS/toluene solution film: S_1 region 7–10 nm and S_2 region 28–30 nm (b) 2.0 wt % SIS/toluene solution film: S_3 region 24–26 nm and S_4 region 30–32 nm, and (c) 3.0 wt % SIS/toluene solution film: 54–57 nm. The (d) image shows the coexistence of different morphologies depending on film thickness. Scan size $3 \times 3 \mu\text{m}^2$.

Playing with different thicknesses in a same film, an unusual distribution of different morphologies as that shown in Figure 3(d) can be achieved: a heterogeneous surface with terrace formation, in which different morphologies such as worm-like, tilted

cylinders, or perforated lamellae along the surface do coexist. Depending on film thickness, interactions between substrate surface and domains will vanish through film thickness, thus resulting in different morphologies. Therefore, for thin films different morphologies can be achieved. However, for thick films only surface parallelly oriented PS cylinders do exist.

SIS films in HOPG substrates

The boundary conditions for SIS thin films in HOPG substrate are quite different when compared to silicon substrate. The most important difference between silicon and carbon substrates is their different affinities with copolymer blocks. In the case of the silicon wafer, due to the higher substrate selective affinity for PI block, the layer close to the substrate was mainly formed by PI block. Instead, the interfacial interactions of both domains with HOPG substrate are nearly similar. Figure 4(a–d) images show AFM characterized SIS films with different thicknesses on HOPG substrate. Figure 4(a) shows a not completely formed film (indicated by arrows) in several regions of the surface. The film exhibiting 9–10 nm thickness corresponds more or less to PS half-cylinder diameter into PI matrix. Therefore, PI and PS location in the substrate seems to confirm the above proposed conformation for SIS thin films in carbon substrate. Figure 4(b) shows a morphology composed by long cylinders parallelly aligned to substrate for a film thickness of 31–33 nm. Thus, using theoretical approach it is possible to conclude that this film was composed by uniform double layers. Nevertheless, Figure 4(c) shows a heterogeneous surface with terraces of different thickness. The C_1 region (34–36 nm) was composed by two layers of parallelly aligned cylinders. However, in the C_2 region (23–25 nm) the film displayed perforated lamellar arrangements. The outermost layer was formed by PI domains whereas the substrate close layer was composed by both domains. PI domains would have volume fraction depletion in the layer below the surface whereas PS would become the majority component driving a phase inversion from PS cylinders crossing the PI matrix to PI cylinders crossing PS matrix.^{5,27} Finally, Figure 4(d) shows a morphology of cylinders parallelly oriented to the substrate homogeneously distributed in the surface. Considering the distance between layers, this film with 58–60 nm is composed by three cylinder layers. Increasing film thickness (not shown in the present work) similar results were obtained. These results suggest that in thick films interactions between substrate and domains located at the film surface are too weak to affect the copolymer surface morphology. Therefore, it is possible to conclude that

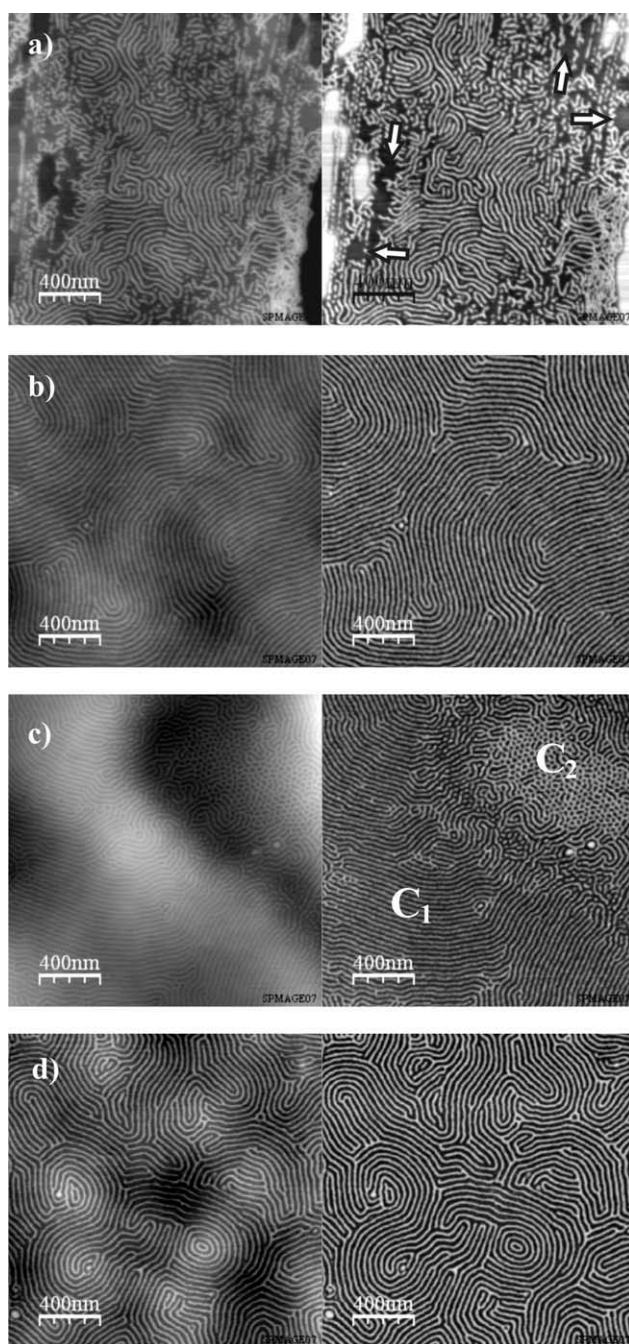


Figure 4 AFM height (left) and phase (right) images of SIS/toluene thin films with different concentrations on HOPG substrate. Films show different morphologies depending on the region. Region thickness: (a) 1.0 wt % SIS/toluene solution film 9–10 nm, (b) 1.5 wt % SIS/toluene solution film 31–32 nm, (c) 2.5 wt % SIS/toluene solution film C₁ region 34–36 nm and C₂ region 23–25 nm (d) 4.0 wt % SIS/toluene solution film: 58–60 nm. Scan size 3 × 3 μm.

substrate parallelly oriented PS cylinders are the most stable morphology in bulk independent of the substrate used. In case of SIS films in carbon substrate, the film thicknesses follow the theoretical approach for asymmetric system. Therefore, the

proposed film conformation for SIS in HOPG substrate was appropriate.

CONCLUSIONS

SIS thin films with different thicknesses were examined in silicon and carbon substrates. CA and AFM analysis revealed different SIS arrangements depending on the employed substrate. On the other hand, considering the different compositions in the layer close to the substrate for silicon and carbon substrates, two different arrangements were suggested. Topographic images and force analysis confirmed those arrangements. SIS thin films showed different surface morphologies such as worm-like, cylinders, and perforated lamellae in both substrates. However, for thicker films, SIS showed cylindrical surface morphologies. Films with thicknesses that did not keep the domain space commensurability showed terraces formation with perforated lamellae morphology in both substrates. This formation seems to be caused due to PI domain depletion in the film interlayer. Homogeneous layers with cylindrical morphology were found for both substrates in films with enough thickness. This morphology is the most stable for the used SIS in bulk, being independent of the employed substrate.

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