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**Nanostructuring of self-assembled poly(styrene-*b*-isoprene-*b*-styrene) block copolymer thin films in a highly oriented pyrolytic graphite substrate**

Iñaki Zalakain, Jose Angel Ramos, Raquel Fernandez, Haritz Etxeberria and Iñaki Mondragon\*

Group 'Materials + Technologies', Escuela Politécnica, Dept of Chemical & Environmental Engineering, Universidad País Vasco/Euskal Herriko Unibertsitatea.

Pza. Europa 1, 20018 Donostia-San Sebastián, Spain

\*Corresponding author. Tel.: + 34-943017177; Fax: +34-943017200

E-mail address: [inaki.mondragon@ehu.es](mailto:inaki.mondragon@ehu.es) (I. Mondragon)

**ABSTRACT**

Highly oriented pyrolytic graphite (HOPG) is a useful substrate to visualize epitaxial formation due to its crystallographic structure. The morphology of a poly(styrene-*b*-isoprene-*b*-styrene) block copolymer thin film on a HOPG substrate was investigated by atomic force microscopy. Block copolymer domains generated a morphology with triangular regularity. This arrangement was induced by the HOPG substrate structure due to van der Waals attraction between the HOPG  $\pi$ -conjugated system and aromatic ring of polystyrene domains. However, increasing the film thickness, the substrate effect on the surface morphology decreased. As a consequence, film surfaces showed the coexistence of different structures such as highly aligned cylinders and perforated lamellae. When film thickness exceeded a threshold value, the substrate did not have effect in the surface arrangements and the surface showed a similar morphology to that existing in bulk.

Keywords: Thin films, Poly(styrene-*b*-isoprene-*b*-styrene), Highly oriented pyrolytic graphite, Epitaxy, Atomic force microscopy, Block copolymer

## 1. INTRODUCTION

The capability of block polymers to self-assemble in a range of 10–100 nm makes them excellent candidates for applications in nanotechnology [1], [2], [3], [4], [5], [6], [7]. Block copolymers are composed of two or more chemically different, and frequently immiscible, polymer blocks covalently bonded together. Thermodynamic incompatibility between blocks generates microphase separation maximizing or minimizing the contact area between blocks [8]. The most relevant parameters in self-assembling are the volume fraction and molecular weight of the blocks, and temperature dependent Flory–Huggins interaction parameter [9], [10]. Depending on these parameters, the block copolymer 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], [2], [3], [4], [5], [6], [7]. The induction of the domains orientation can be achieved by different methods such as electric fields, directional crystallization or confining in physically defined patterns, among other methods [11], [12], [13]. However, few authors have reported block copolymer domain orientations by the epitaxial formation method [14], [15]. The epitaxial formation consists of macromolecule alignments induced by strong interactions between substrate and deposited molecules. Thus, the copolymer domains can be oriented along the crystallographic lattice of the substrate. The atomically flat basal surface of the highly oriented pyrolytic graphite (HOPG) substrate makes possible polymer epitaxial formation [16]. Each carbon atom in graphite has a free electron due to  $sp^2$  hybridized orbitals. Thus, the substrate can interact by  $\pi$ -interactions with deposited molecules [17]. These attractions can induce molecules orientation in two dimensions along graphite crystallographic axes [18]. The epitaxial formation has been extensively researched in different hydrocarbon molecules such as cellulose, alkanes, carboxylic acids, thiols, among others but few times using block copolymers [17].

On the other hand, in block copolymers morphology can also be affected by film thickness [6], [7]. Increasing the film thickness, interactions with the substrate cannot be enough to influence the surface arrangement. In block copolymers, the film thickness is related to copolymer domain characteristic spacing. If the thickness is proportional to the domain characteristic spacing, the film will display a homogeneous surface. However, if the film is not proportional to the domain characteristic spacing, the surface will show islands and holes with different thickness regions

(terraces) [5], [6], [7], [19], [20]. These regions will keep the domain characteristic spacing.

In this work, the poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer has been studied using the HOPG substrate. The obtained morphologies were studied by the atomic force microscopy (AFM) technique. The influence of thickness in the epitaxial formation was analyzed varying the film thickness. The results of this study reveal a triangular microstructure in the thinnest film. However, increasing the film thickness, the substrate has a lower influence giving a variety of arrangements with no sign of epitaxial formation.

## **2. EXPERIMENTAL SECTION**

### **2.1. SAMPLE PREPARATION**

The triblock copolymer used in this study was poly(styrene-*b*-isoprene-*b*-styrene) from Kraton Polymer. The molecular weights of polystyrene (PS) and polyisoprene (PI) blocks are 17,460 g/mol and 40,740 g/mol, respectively. The PS weight fraction in the copolymer is 0.3. The SIS films were prepared on freshly cleaved HOPG substrate. The substrate was dipped into the SIS/toluene solution with a rate of 40 mm/min, and subsequently pulled out of the solution at 5 mm/min. Solutions with the following SIS concentrations were employed: 0.5, 1.0, 2.0 and 3.0 wt.%. Thereafter, the solvent was evaporated for 24 h at room temperature [21]. This SIS copolymer film was self-assembled at room temperature without any annealing procedures [22], [23].

### **2.2. ATOMIC FORCE MICROSCOPY IMAGING**

The surface morphology of the samples was characterized by AFM. Topographic and phase images were obtained with a Nanoscope IVa Dimension 3100 AFM (from Digital Instruments). Tapping mode in air was employed using an integrated silicon tip/cantilever (125  $\mu\text{m}$  in length and with ca. 300 kHz resonant frequency) at a scan rate of 1.0 Hz and a resonance frequency of  $\sim$  300 kHz. The measurements were performed with 512 scan lines. Several regions were scanned obtaining similar results. Analysis of AFM images was carried out with a WSxM software (Nanotech Electronica). A 2-dimensional fast Fourier transformation (2D-FFT) was performed via the WSxM software. For measuring film thickness the 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.

### 3. RESULTS AND DISCUSSION

AFM was used to analyze the morphological behavior of SIS block copolymer on HOPG substrate. The surfaces of four different films obtained from SIS/toluene solutions with different concentration were examined. Surface coverage varied according to the solution concentration. As shown below, increasing the film thickness, the block copolymer shows different arrangements. Fig. 1 shows topographical and AFM phase images of the film dip cast from the SIS/toluene 0.5 wt.% solution. The measured film thickness was  $< 6$  nm. The AFM image of the adsorbed SIS copolymer film shows highly aligned polymer segments. The image displays not randomly distributed domains connected between them with a triangular regularity. The molecular arrangements adopted a parallel alignment with a cross-angle of  $120^\circ$ . The 2D-FFT diagram of the AFM image, shown in Fig. 2, confirmed this result. The diagram displays a hexagonal pattern where three components crossed at  $120^\circ$  between them were seen, similar to obtained by Yokota et al. [24]. This result suggests the epitaxial formation of the block copolymer where copolymer domains are aligned along the HOPG substrate. To explain this behavior, it is necessary to consider that the HOPG crystal lattice has a layered structure, where each graphene layer is composed by a planar arrangement of fused hexagonal benzene rings, as shown in Fig. 3. In the case of the upper graphene sheet (the sheet in contact with the air), two types of carbons do exist: carbons interacting with carbons of other sheets ( $\alpha$ -carbons) and not interacting carbons ( $\beta$ -carbons) [16].  $\alpha$ -Carbons interact with adjacent carbons but  $\beta$ -carbons possess free electrons with capability to interact with deposited molecules. The angle between those  $\beta$ -carbons is  $120^\circ$ . Thus, strong  $\pi$ - $\pi$  interactions between the delocalized  $\pi$  electrons of PS phenyl groups and the  $\beta$ -carbons of the HOPG substrate can generate the macromolecule orientation [17]. This assumption suggests that the domains with a triangular regularity correspond to polystyrene blocks.

Fig. 4a–c presents AFM images of different films cast from SIS/toluene solutions with several concentrations. For the 1 wt.% solution, Fig. 4a, even if some non-covered regions were present in the film, interestingly, depending on the thickness of each region the surface exhibited two types of cylinders. The film showed well-defined

cylinders in slightly thicker regions (10–12 nm), whereas in slightly thinner regions (7–8 nm) the cylinders had smaller length and height and were oriented in a common direction, as indicated by the arrows. Those results suggest that for a block copolymer exceeding a film thickness, the surface morphology does not show epitaxial formation, being independent of the employed substrate.

Surface morphology changed for increasing SIS concentration. Fig. 4b shows the coexistence of perforated lamella ( $S_1$  regions, 30–32 nm) and long cylinder ( $S_2$  region, 24–26 nm) morphologies for the film cast from the 2.0 wt.% solution. Perforated lamella morphology is generated by a transition between two stable layers [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24], [25]. This morphology is caused by PI domain segregation in both interfaces (substrate and air), driving its depletion in the layer below the surface. Therefore, PS would become the minor component and PI the major one, thus leading to the formation of the PS matrix perforated by PI cylinders.

Finally, Fig. 4c shows AFM images of the thickest film (54–57 nm) cast from the 3 wt.% solution. In this case, the images show a homogeneous surface composed by randomly oriented polystyrene cylinders without sign of orientation. The surface morphology was not affected by the HOPG substrate, as it was similar to that obtained in bulk (not shown in the present work). These results confirm that in block copolymer films beyond a thickness threshold value, interactions between HOPG substrate and block copolymer chains are not able to affect domain orientation in the film surface.

## CONCLUSIONS

The domain alignment of SIS thin films deposited in the HOPG substrate showed clear dependence on film thickness. For films with very low thickness, the copolymer showed a morphology with a triangular regularity. This arrangement was induced by van der Waals attractions between free electrons of delocalized  $\pi$  orbitals of graphene  $\beta$ -carbons and aromatic rings of polystyrene domains. Increasing film thickness, domain orientation on the film surface decreased only showing some order along a common direction. For film thickness exceeding a threshold value, film surface morphology displayed the bulk morphology without signs of interactions between substrate and block copolymer domains.

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## Figure captions

**Fig. 1** AFM height (left) and phase (right) images of a film dip cast from the SIS/toluene 0.5 wt.% solution on the HOPG substrate. Image size:  $3 \times 3 \mu\text{m}$ .

**Fig. 2** 2-D fast Fourier transformation corresponding to the topography image of the film dip cast from the SIS/toluene solution with a 0.5 wt.% SIS concentration.

**Fig. 3** The spatial projection of the HOPG substrate. Top sheet carbons (dots) are connected to each other by grey lines and the carbons of the second sheet by black lines. The different carbons  $\alpha$  and  $\beta$  are signed in the picture.

**Fig. 4** AFM height (left) and phase (right) images of films dip cast from SIS/toluene on the HOPG substrate with the following SIS wt.% concentrations: a) 1.0, b) 2.0 and c) 3.0 wt.%. Image size:  $3 \times 3 \mu\text{m}$ .