

# Soft-lithography of ordered block copolymer nanostructures

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Block copolymers have attracted much attention since they can be applied to create micro and nanoscale structures because of the different aggregation structures that compose them. Proposed is a route to create templates from poly(styrene)-b-poly(ethane-co-butene)-b-poly(styrene) (SEBS) nanostructures to be used in patterning surfaces, electrodes or thin polymer films. A thin liquid film of SEBS/toluene solution was deposited by a dip-coating procedure and, after the solvent evaporation, SEBS ordered structures were spontaneously displayed in a hexagonal arrangement. The moulding template (a negative copy of the prime SEBS structures) was made of polydimethylsiloxane (PDMS) and lastly a replica in epoxy was successfully achieved and the original hexagonal pattern was formed with reasonable accuracy. All structures were studied by atomic force microscopy images in tapping mode. The SEBS nanostructures were characterised with a diameter (height) of 914 nm (38 nm) whereas with the PDMS template it was 749 nm (29 nm). The epoxy replica presented a diameter (height) of 553 nm (21 nm). All the process (nanostructure, template and replica) showed 80% fidelity when compared with the previous step, demonstrating the possibilities of using this lithography process as an efficient patterning tool of electrodes and film surfaces.

**1. Introduction:** Block copolymer has attracted interest among researchers for the development of ordered and well organised sub-micrometric structures, as it can be applied in several areas such as the synthesis of nanoparticles [1], lithography processes for nanostructures patterning surface and electrodes [2–6], drug delivery devices [7] etc., and has become an important tool for the development of systems at nanoscale. This unique property that makes block copolymer so important and special in producing sub-micrometric structures is related to the phase segregation of their constituents forming molecule blocks covalently linked [8, 9]. Depending on the way which the blocks are linked (linear, branched, star-like or cyclic) and the nature of the interactions between the blocks (coil–coil, rod–coil and semi-crystalline–coil), different morphologies can result, such as lamellae, gyroid, spheres or cylindrical. These various block copolymer systems can self-assemble to form different microphases showing different behaviours in solutions, and bulky and thin films.

Block copolymer thin films have already been studied by both theoretical and experimental researchers [10, 11]. The morphologies obtained by thin films can be tuned by chemical treatment, by the deposition of a hydrophobic or a hydrophilic layer on the substrate surface or can be tuned by applying external fields such as electrical, mechanical or thermal [12]. For well-diluted block copolymer solutions, the dewetting process appears to drive the way the film is deposited over the substrates surface. Instability processes (Rayleigh instability) concomitantly with solvent evaporation (Marangoni effect) can play an important role on the ordered nanostructures deposition. The wetting/dewetting competition drives the thin film rupture, resulting in attractive and repulsive interactions. The excess of intermolecular interaction free energy can be theoretically expressed as

$$\Delta G = -\frac{A}{12\pi L^2} + S^p \exp\left(\frac{-L}{l}\right) \quad (1)$$

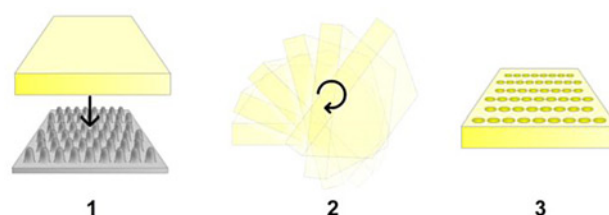
where  $A$  is the effective Hamaker constant (associated with non-polar intermolecular interactions),  $S^p$  is the polar component of the spreading coefficient,  $L$  is the film thickness and  $l$  is the correlation length.  $\Delta G$  may be expressed by the balance of interfacial

tensions as  $S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}\cos\theta$  (spreading coefficient) where  $\theta$  is the contact angle between the  $\gamma_{sl}$  and  $\gamma_{lv}$  surface tensions.

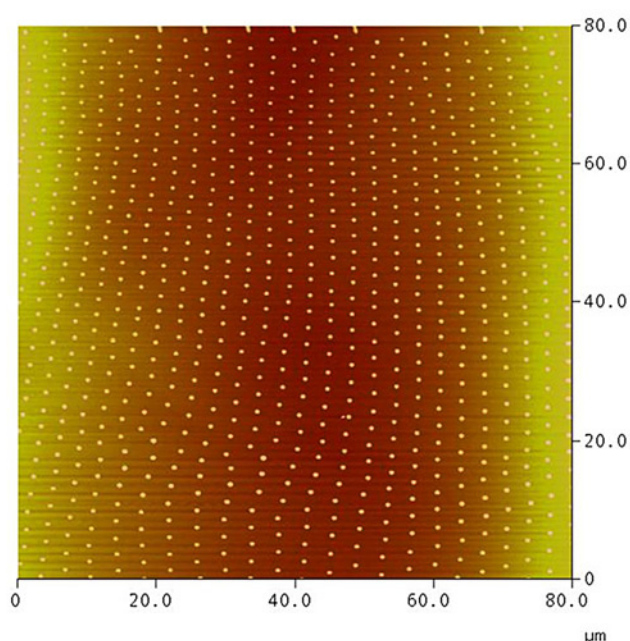
The use of block copolymer as raw material for the production of nanoscale structures appeared as an alternative route to overcome the challenges imposed by photolithography, concerning its limitations because of optical physics. As a new lithography technique, soft-lithography uses an elastomeric mould to copy the prime nanostructures and yield a master template used as a patterning tool. The elastomeric material is usually polydimethylsiloxane (PDMS), the advantages of which are: (i) its flexible backbone enables accurate replication of relief shapes of the patterning elements; (ii) its low Young's modulus and low interface energy (21.6 mJ/m<sup>2</sup>) enable conformal contact between surfaces without applying pressure, and the non-destructive detachment from patterned structures; and (iii) its commercial availability in bulk quantities at low cost.

In this Letter we propose a route to a lithography process at micro and nano scales utilising a block copolymer to generate well-ordered structures over mica surfaces. The production of a PDMS template follows, and so the replication of block copolymer nanostructures in epoxy resin as the final goal is achieved.

**2. Experimental procedures:** Commercial G 1560 Kraton poly(styrene)-b-poly(ethene-co-butene)-b-poly(styrene) (SEBS) triblock copolymer with a weight ratio of 15(S):70(EB):15(S) was used to form the self-organised structures. Gel permeation chromatography in THF solution with polystyrene standards was used to characterise the commercial SEBS, from which the values



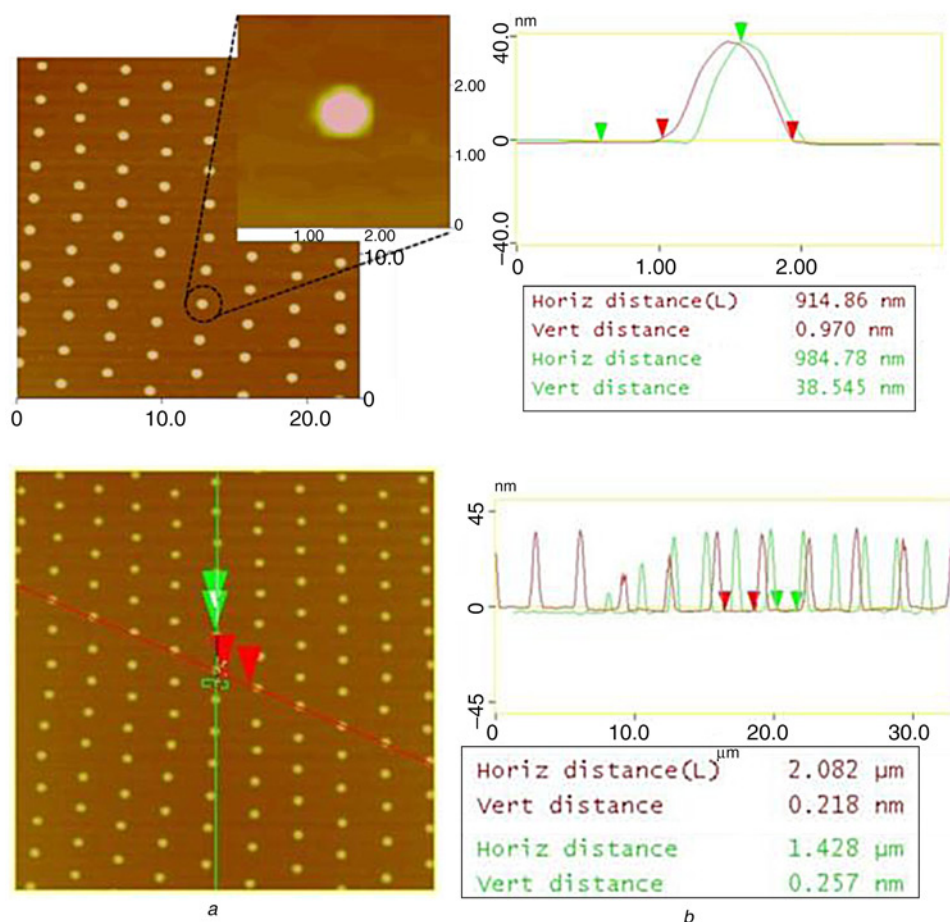
**Figure 1** Soft-lithography process used to copy the triblock copolymer nanostructures



**Figure 2** AFM height image  $80 \times 80 \mu\text{m}$  of self-organised nanostructures over mica substrate  
The SEBS nanostructures are hexagonally organised and are characterised by the same size and interspacing between the structures

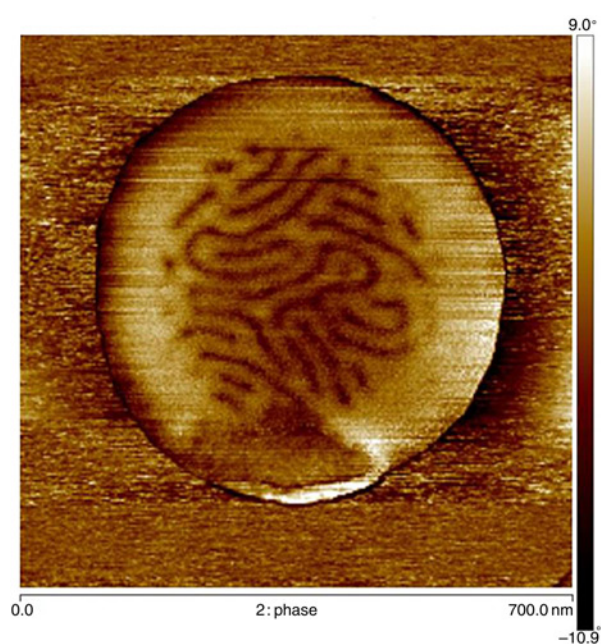
$M_w = 112\,000 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.15$  were obtained. As solid substrate we used pre-cleaved mica because of its very low roughness and because of its relatively chemically inert surfaces. The SEBS triblock copolymer was dissolved in toluene forming a diluted solution ( $\sim 0.125 \text{ g l}^{-1}$ ) in which a layer of mica was plunged for a few seconds. As a result of this dip-coating, the entire mica surface was covered by a thin liquid layer. This procedure was carried out in environmental conditions with temperatures between  $20^\circ$  and  $25^\circ\text{C}$  and relative humidity between 30 and 40%. The PDMS Sylgard 184 of Dow Corning was used as material in the soft-lithography process to create a master mould. To replicate the master mould, a bi-component adhesive epoxy (Araldite from Brascola Co.) was chosen, considering its simplicity and easiness to detach from the elastomeric mould. The whole process was characterised by tapping-mode atomic force microscopy (TM-AFM), simultaneously obtaining height and phase imaging data. All the physics phenomena underlying the ordering and formation of the SEBS nanostructures were explained in previous published works [13–15].

The nanostructures deposited on mica by the dewetting of the copolymer solution were used to produce the PDMS master mould template. The PDMS was drop casted over the nanostructures on the mica surface (step 1 in Fig. 1) and thermally treated at 340 K for 4 h, producing a negative copy of the nanostructures on the PDMS, as illustrated in Fig. 1 (step 3). Lastly, a replica was produced in epoxy by casting it over the PDMS template and letting it dry for 24 h.



**Figure 3** Nanostructure profile and interspacing of dots characterised by AFM tapping mode  
*a* Image of dots nanostructures presenting diameter (height) of 914.8 (38.5) nm  
*b* Interspacing between the nanostructures





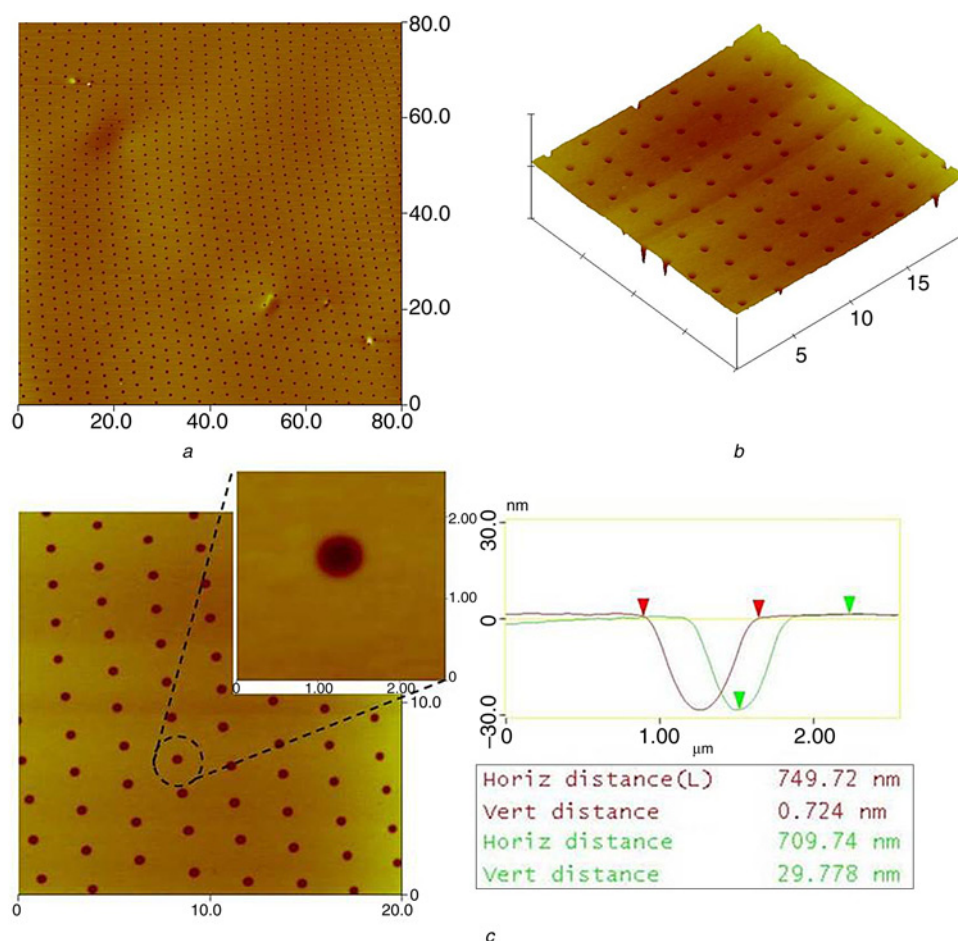
**Figure 4** AFM phase image of the SEBS nanostructure  
Lamellar morphology is formed due to the segregation of different building blocks of the triblock copolymer

**3. Results:** As previously reported by Carvalho *et al.* [13], the self-organised SEBS nanostructures depend on the concentration of the triblock copolymer solution. For non-diluted solutions

(10 g.l<sup>-1</sup>) the deposited thin films cover the entire substrate, and for diluted solutions (0.1 g.l<sup>-1</sup>) a homogeneous thin film (liquid thin film < 100 nm) is formed. The dewetting takes place because of the negative spreading coefficient ( $S < 0$ ) breaking up the thin film into droplets (Rayleigh instabilities). Very regular and homogeneous block copolymer structures are deposited, and they are characterised by their regularity in shape and interspacing distance between the nanostructures.

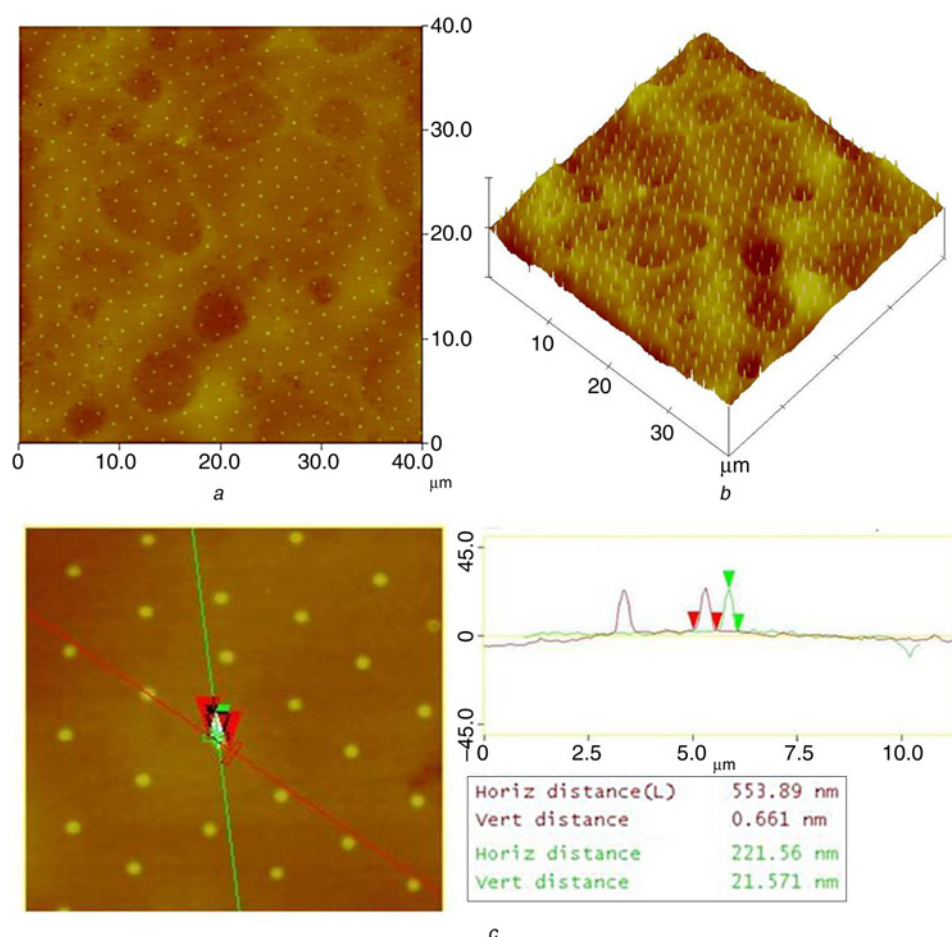
Figs. 2 and 3 represent a measurement performed on AFM. The height image obtained in AFM tapping mode quantifies the dimensions of the SEBS structures and the distance to their nearest neighbours as presented in Fig. 3a. Their diameter (height) measurements presented values of 918.7 nm (38.5 nm). The nanostructures interspacing (the nearest neighbours) are located at 1.5  $\mu\text{m}$  along the 0y direction and 2.1  $\mu\text{m}$  along a straight line at ( $\pi/m$ ) degrees to the vertical direction (Fig. 3b). It is worth mentioning that this regularity is not over the entire substrate, for some regions are disordered as a consequence of the dewetting and the instability processes responsible for the SEBS deposition over the substrate's surface as previously reported [13].

Owing to the existing physical and chemical incompatibility between the different building blocks of the copolymer, this material tends to self-organise in a variety of ordered nanostructures through the phase segregation. This segregation may lead to the formation of different microphases. Considering the bulk state, nanostructures can be formed with uniform morphologies in the shapes of cylinders, spheres and lamellae. Fig. 4 represents an AFM phase image of the SEBS nanostructures. We can identify a lamellar morphology formed by the rigid part of the triblock copolymer (polystyrene, represented by the dark portion in Fig. 4) and the



**Figure 5** Negative copies of SEBS nanostructures in PDMS

The PDMS forms a copy of the original SEBS structures as indicated in Figs. 5a and b with accuracy in shape and dimensions, as demonstrated in Fig. 5c



**Figure 6** Replica in epoxy resin of SEBS nanostructures

Owing to inner stresses the replica surface (Figs. 6a and b), presents higher roughness when compared with the PDMS mould. Even so, the mimicked SEBS structures are obtained with diameter (height) of 553.9 (21.6) nm, as presented in Fig. 6c

elastomeric part of the triblock copolymer (poly(ethene-co-butene), represented by the white portion in Fig. 4).

The master mould was successfully obtained with PDMS having no destructive detachment of the deposited nanostructures over the mica substrate. The master mould copies the nanostructures dimensions with great accuracy ( $\sim 82\%$ ) as a consequence of the low PDMS interface energy and Young's modulus. The SEBS structures' negative copies in PDMS can be clearly seen in Figs. 5a and b. Fig. 5b represents a 3D image of holes in the PDMS (the copied nanostructures) indicating that the PDMS can form a smooth and regular surface (RMS roughness = 3.2 nm) which can be easily detached from the mica substrate and from the SEBS nanostructures. The profile analysis in Fig. 5c quantifies the PDMS diameter (height) of 749.7 nm (29.8 nm).

The replication process results are shown in Fig. 6. The analysis of the replica surface was characterised by its roughness (10.1 nm) showing values higher than the PDMS mould's. It is clearly evident, as presented in Fig. 6b, that the resin surface morphology is not as flat and smooth as the template is. Defects on the surface seem to compromise the process reliability affecting directly the height of the copied SEBS structures on the replica process. The replica structures presented peaks of 21.6 nm and a diameter of 553.9 nm, as shown in the profile data of Fig. 6c. These defects appear, we believe, as a result of a non-homogeneous mixture of the resin and its catalysator, making some regions dry faster than others, and so creating inner stresses that cause holes on the surface. To avoid defects like these, improvements in replica material are required, keeping in mind the necessity of a non-destructive detachment of the master mould.

Longaresi *et al.* [15] have recently published a computational study of ordered SEBS nanostructures, template and replica based on hexagonality indexes and the radial distribution function. The computational study was based on analysis of AFM images identifying the neighbourhood of each dot (nanostructure) by using Delaunay triangulation [16]. The results showed that the number of defects (nanostructures that break the hexagonal symmetry) does not increase significantly with the replication procedure, maintaining the local ordered arrangements. In addition to the studies of Longaresi *et al.*, the characterisation of the shapes and sizes of structures in the whole process by AFM images have demonstrated that the soft-lithography procedure proved to be a highly reliable, fast and easy procedure to replicate nanostructures.

**4. Conclusion:** In this Letter a new route to the lithography process at nanoscale is proposed. As a result, self-organised triblock copolymer nanostructures were produced by dip-coating over mica substrate followed by a master mould production and replication process. The master mould is the key to the soft-lithography process, where we can use this mould with copied nanostructures to pattern surfaces or in a replication process for further patterning. Regarding the replication process, structures with characteristics similar to the prime SEBS nanostructures were obtained. For the whole process – the SEBS nanostructures, the PDMS mould production and the replication process – we can state that each process had a fidelity of 80% of the former structures. This work can be applied to improving the architecture of polymeric devices, and patterning electrodes and

thin films featured with nanoscale dimensions using the mould or the replica (like a stamp) in a surface patterning process [17–20].

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## 6 References

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