Microphase Separation of Block Copolymers: SBS

AFM has emerged as a useful method for studies of nano-scale domain morphology of block copolymers – the polymer materials, in which chemically-different components segregate in various phases. This morphology is key for structure-property relation, and its visualization with TEM requires an intricate preparation with selective staining. The alternative approach was proved in AFM studies of triblock copolymer of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), see references below. This material consists of soft and hard components, this helps the visualization of dissimilar blocks in AFM images. Spin-cast SBS film on Si substrate is a useful sample for learning AFM imaging of soft material and compositional mapping.

Non-destructive imaging of SBS film in contact mode requires the use of a soft probe (k< 10 mN/m) **Figure 1a-c.** Sample surface is smooth with height corrugations in the 1-2 nm range, and nanoscale grains and short ribbons are seen at small scale.

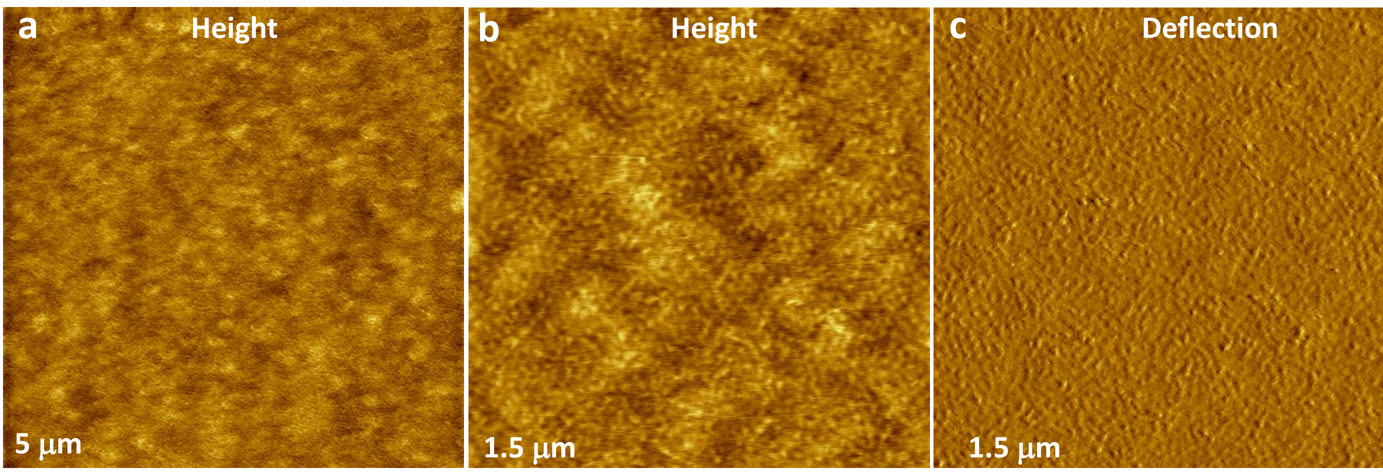

Figure 1a-c. Height and deflection images of SBS film in contact mode.

A distinction of components in heterogeneous samples in contact mode is possible with lateral force contrast, which is related to local friction. Such contrast is noticed in **Figure 2a-b**. A tip-force increase by altering the deflection set-point leads to surface dents at the scan borders, **Figure 2c**.

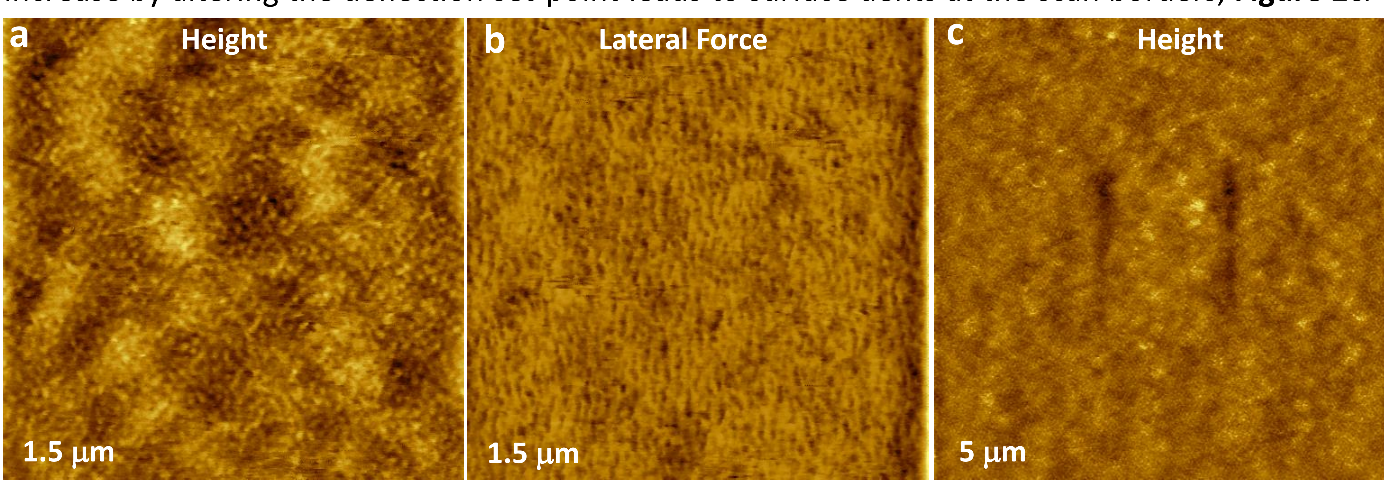

Figure 2a-c. Height and deflection images of SBS film in contact mode.

R. van den Berg, H. de Groot, M.A. van Dijk, D.R. Denley "Atomic Force microscopy of thin triblock copolymer films" *Polymer* **1994**, *35*, 5778-5781.

S. Magonov, J. Cleveland, V. Elings, D. Denley, M.-H. Whangbo "Tapping-mode atomic force microscopy study of the near-surface composition of a styrene butadiene-styrene triblock copolymer film" *Surface Science* **1997**, *389*, 201-211.

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Limitations of contact mode use on soft materials, made AM-PI (aka tapping) mode common for studies of block copolymers. Low-force imaging is needed to achieve accurate surface profiling. High-force operation reveals local stiffness and adhesion changes thus discerns dissimilar spots or components. As the tip and sample come into periodical contact, the peak force becomes larger with increase of initial oscillation A_0, and decrease of set-point amplitude A_{sp}. Here we assemble height and phase images of an SBS film, which were recorded at different amplitudes using Si probes with k = 0.084 N/m, k = 1.93 N/m and k = 23.0 N/m. The surface composition affects the image contrast and what structural information can be obtained from such measurements. In many cases phase images exhibit a higher contrast than height images that better reveals surface composition. The images obtained with the soft probe at A_{sp}= 8 nm, A_0 = 10 nm are shown in **Figure 3a-c**. The amplitudes' variations (limited due to the probe stickiness) did not change the contrast.

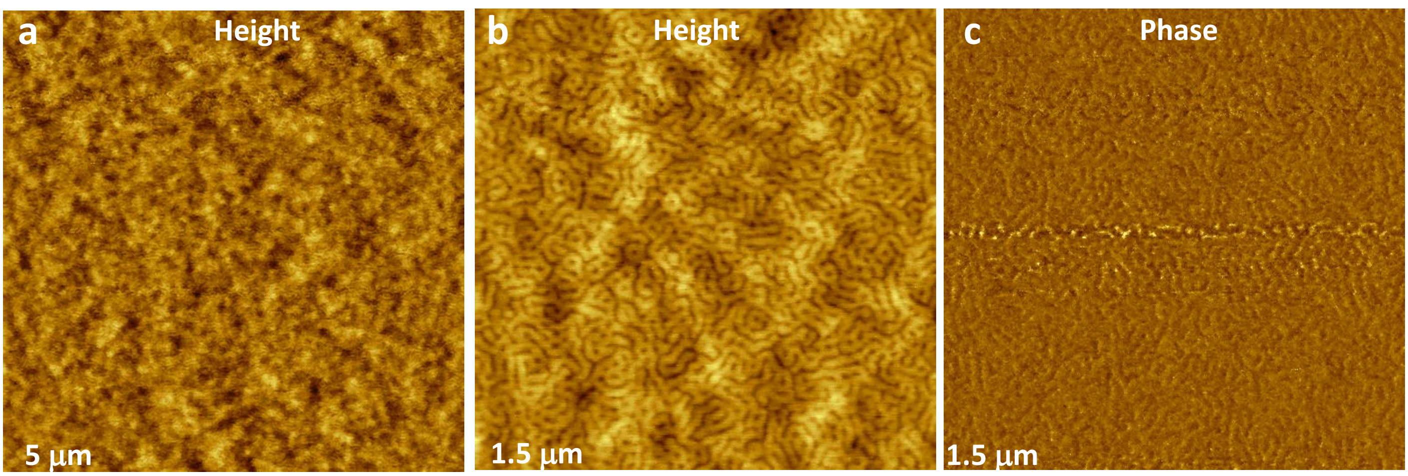

Figure 3a-c. Height and phase images of SBS film in AM-PI mode with Si probe (k = 0.065 N/m)

Imaging with the stiffer probe (k = 1.93 N/m) and low force (A_{sp} = 18 nm; A_0 = 20 nm) led to the height and phase patterns with height corrugations of 3 nm and phase changes of 3 degrees, **Figure 4a**. At high force (A_{sp} = 12 nm, A_0 = 50 nm) the images have changed (**Figure 4a-c**) with 10-fold increase of the contrast. This is related to a transition from attractive to repulsive force regime, as judged by the overall phase level (not shown here).

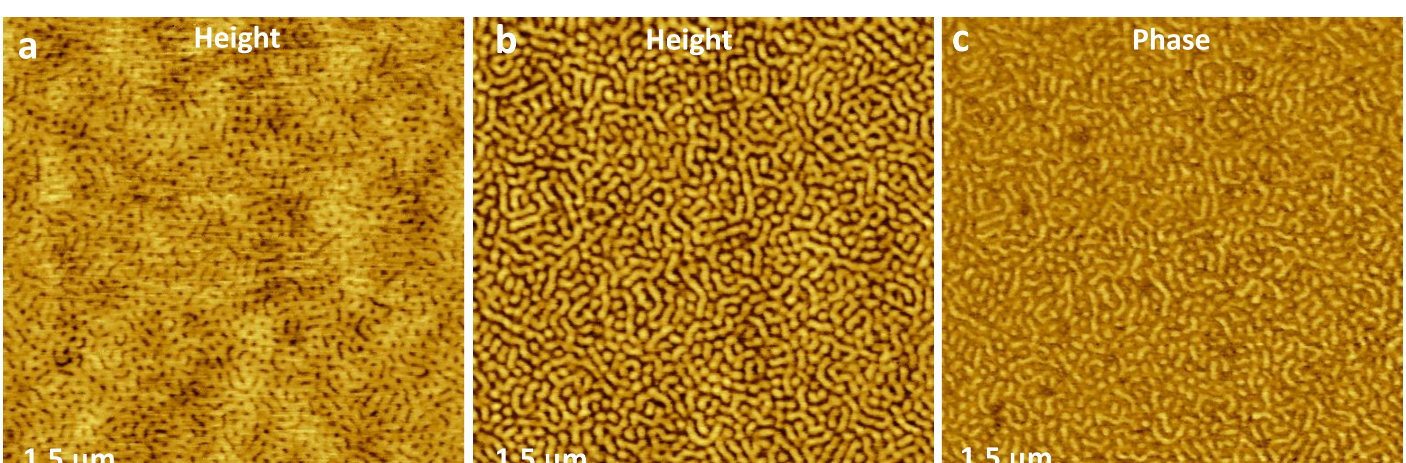

Figure 4a-c. Height and phase images of SBS film in AM-PI mode with Si probe (k = 1.93 N/m)

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A variety of patterns was observed in the images recorded with stiff probe (*k* = 23.0 N/m) and A_0 = 6 nm and 24 nm. By setting A_{sp} around $0.5A_0$ the peak force can reach, respectively, 1.7 nN and 7.8 nN according to our estimates made for polystyrene with 3GPa elastic modulus (S. Belikov et al *Mater. Res. Soc. Symp. Proc.* **2013**, Vol. 1527, DOI: 10.1557/opl.2013).

At low-force conditions, when A_{sp} is close to A_0, the height and phase images are practically identical for both A_0, **Figure 5a**, **6a**. The phase images (**Figure 5b** and **Figure 6b**) mimic the height patterns with better contrast in **Figure 5b**. Therefore, the images, which were obtained at low force present surface topography of SBS film, which reflects microphase separation of dissimilar blocks.

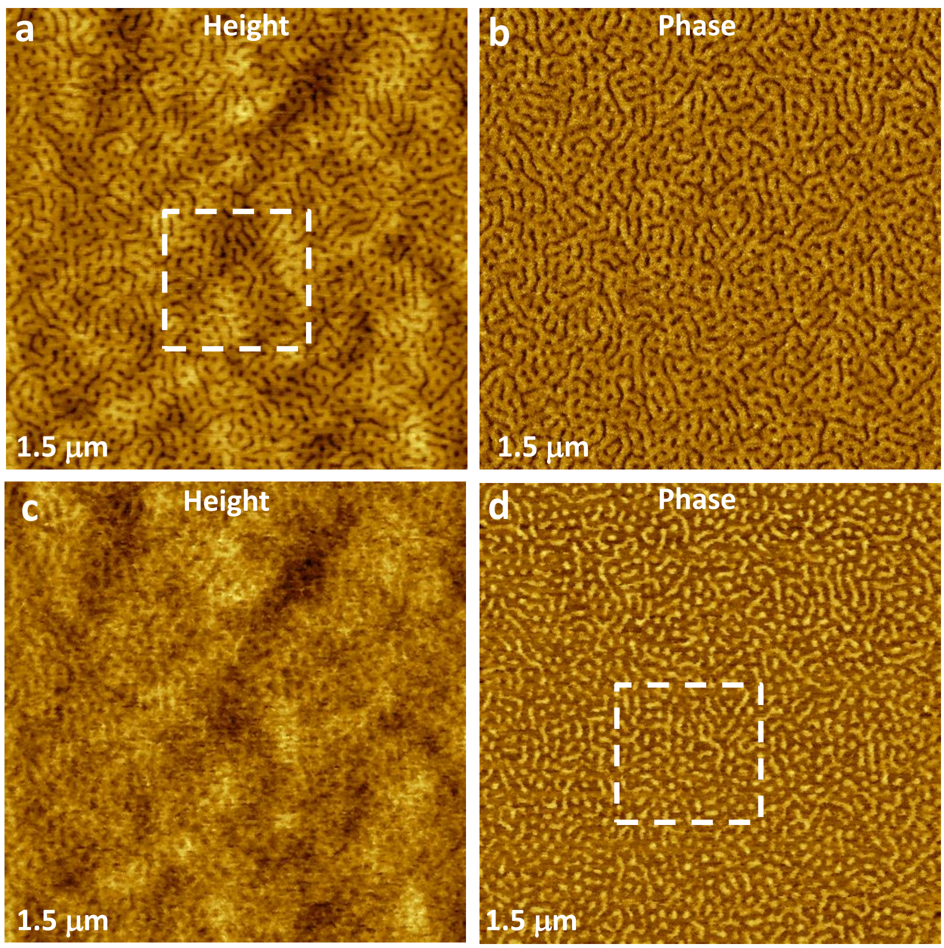

Figure 5a-d. Height and phase images of SBS film in AM-PI mode with Si probe (*k* = 23 N/m) and A_0 = 6 nm.

Visualization of sample morphology based on differences of the probe force interactions is realized in imaging with higher force. At A_{sp}~$0.5A_0$ height images have drastically changed, **Figure 5b**, **6b**. The height pattern of **Figure 5b** became less obvious but it still reflects the microphase separation morphology due to an alternative contrast of nanoscale structures. Simultaneously recorded phase image (**Figure 5c**) exhibits well pronounced pattern with a contrast reversed to that of **Figure 5a** (see the areas marked with the dashed white squares).

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The contrast of height and phase images **(Figure 6c-d**), which were recorded at the peak force of 7.8 nN, also show the identical contrast pattern that is reverse to one in the low-force height image, **Figure 6a.**

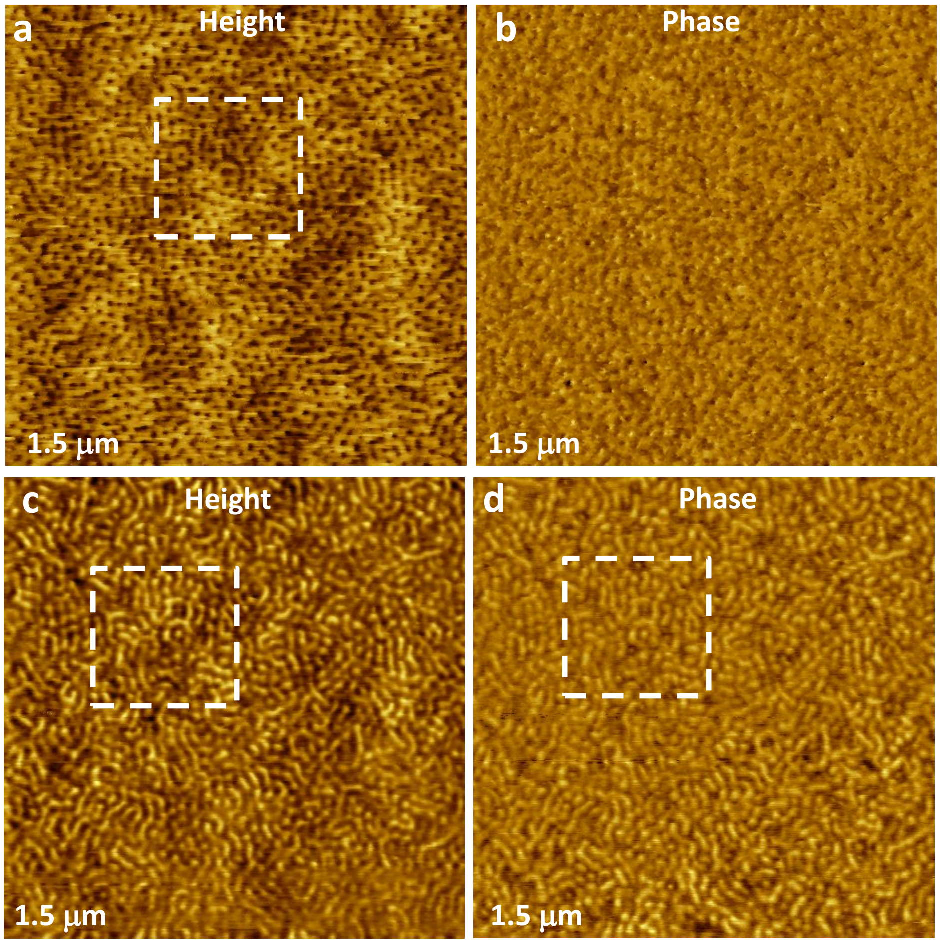

Figure 6a-d. Height and phase images of SBS film in AM-PI mode with Si probe (k = 23 N/m) and A_0 = 24 nm.

A variety of height and phase images obtained in AM-PI mode with different probes at various tip-forces has revealed the microphase separation pattern of SBS film with averaged periodicity around 34 nm. The assignment of the height and phase features to individual polystyrene and polybutadiene blocks is quite challenging. The help might come from studies of this sample in D-CNT mode (aka PeakForce™), which can provide maps of elastic modulus differentiating soft PB and hard PS domains.