

# A multi-wall carbon nanotube (MWCNT) relocation technique for atomic force microscopy (AFM) samples

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## Abstract

A simple relocation technique for atomic force microscopy (AFM), which takes advantage of multi-wall carbon nanotube (MWCNT), is used for investigating repeatedly the imaging of some specific species on the whole substrate with a high relocation accuracy of tens of nanometers. As an example of the application of this technique, TappingMode AFM ex situ study of the morphology transition induced by solvent treatment in a triblock copolymer thin film has been carried out.

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## 1. Introduction

The atomic force microscopy [1] (AFM) has been proven to be a useful tool for visualization of surface topography at the nanometer scale. In comparison with other surface instruments such as electron microscopy and field ionic microscopy,

AFM is much more widely used in the study of soft samples such as polymers [2–7] and biological systems [8–13]. One of the main limitations with the AFM is that it is difficult or even impossible to relocate the same feature, object or the region of interest within a sample once the probe tip is lifted or the substrate is rotated or moved. A high-precision relocation technique is needed for a great many applications. One of the most important applications of the AFM is in the research of changes in the samples. This is delineated in a lot of research works on polymer transitions [14–17] and biological processes [18,19], especially in

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research of the different morphology transitions of block copolymer thin films caused by either solvent or annealing treatment.

For example, in the *ex situ* AFM study of morphology evolution, in order to observe and compare microdomains of block copolymers, it is necessary to zoom in an area at about  $1.5 \times 1.5 \mu\text{m}^2$  scale and precisely relocate the same spot later again after treating the sample. This is obviously a tedious and challenging task. On the other hand, if the morphology of the block copolymer has been changed completely after a certain treatment, some extra clues independent of microdomain patterns are needed. Otherwise there is no way to find the previous imaged spot.

In the pioneering work of Markiewicz and Goh [2], they utilized a suitable marker that could be mounted under the semi-transparent substrate as a routine relocation method in AFM. Although the method could sketchily locate the sample, it was time consuming and its relocation precision was not very high (about tens of micrometers). Hahn et al. [16,17] used specially made substrate in order to perform the *ex situ* AFM study of morphology evolution in a PS-*b*-PMMA block copolymer thin film under annealing conditions. However, it is not easy to make the special substrate. In this paper, we report a relatively efficient and simple relocation technique achieved by two kinds of home-made markers to perform an AFM *ex situ* study of morphology development induced by solvent treatment in a triblock copolymer thin film. This method can be used in AFM *ex situ* studies of various soft samples such as polymers and biological systems. The relocation accuracy can reach tens of nanometers.

## 2. Experimental section

### 2.1. Materials

The poly(styrene-ethylene/butylene-styrene) (SEBS) triblock copolymer coded as Kraton G-1650 was a commercial product of Shell Company. Its molecular weight, polydispersity and styrene content are  $7.5 \times 10^4$ , 1.36 and 27%, respectively [20]. Two solvents, xylene, a good solvent for both

polystyrene (PS) and poly(ethylene/butylene) (PEB) blocks, and alcohol, are used in this work. Multi-wall carbon nanotubes (MWCNTs) were purchased from Shenzhen Nanotech Port Company. A Branson ultrasonic cleaner (B3510E) was used for ultrasonic dispersion of MWCNTs. A Digital Instrument multimode SPM III AFM was used for viewing directly the cantilever and the backside surface features of the mica sheet.

### 2.2. Preparation of samples

The SEBS powders were first dissolved into xylene to prepare 0.3 wt% solution. Film was cast from 0.3 wt% solution onto a freshly cleaved mica substrate and then dried under ambient conditions. Some MWCNTs were dissolved into alcohol and dispersed for 20 min in a ultrasonic cleaner at a frequency of 40 kHz. Then One drop (40  $\mu\text{L}$ ) of the solution was immediately cast (drop casting) onto SEBS film. The sample was imaged by AFM after its surface dried in ambient air.

A piece of filter paper was put into the Petri dish to cover its bottom. The sample was put on the filter paper. After adding 500  $\mu\text{L}$  pure solvent xylene on the filter paper (not on the substrate), the dish was sealed in a closed vessel and kept at room temperature. The sample was taken out at intervals of 0.25 h and measured after drying for few minutes in ambient air. In order to make up for loss of solvent, 200  $\mu\text{L}$  pure solvent xylene was added on the filter paper each time before the sample was put inside the Petri dish for fumigating again.

### 2.3. Relocation procedures

The used mica was cut into an inequilateral pentagon with a tip. In order to prevent the sample from being rotated, the orientation of the tip should be accordant every time. Two sharp crossed scratches were made on the backside of the mica substrate beforehand as mark for relocating the  $5 \times 5 \mu\text{m}^2$  large area (shown in Fig. 1). More similar marks can be made according to the operator's will. Then the mica surface was cleaved and some 0.3 wt% solutions were dropped on it. The sample was dropped with

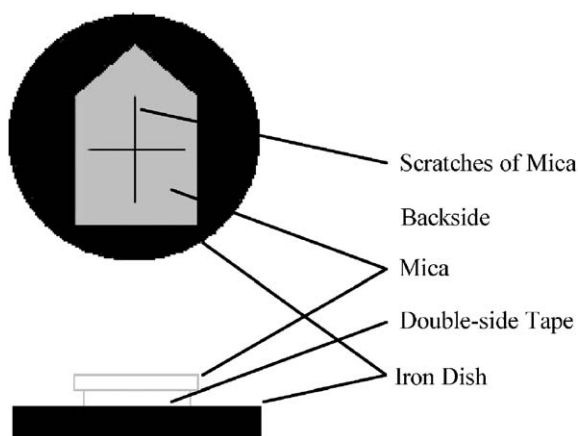


Fig. 1. A mica substrate that was marked by two sharp crossed scratches on the backside as a sample locator, was mounted on an iron sheet by a double-sided tape.

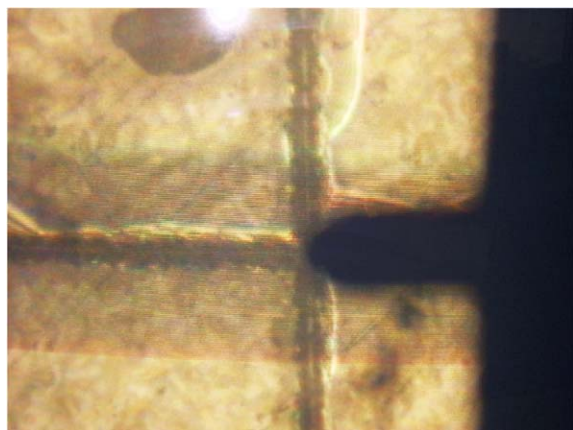


Fig. 2. The focus image of the backside of a mica substrate.

MWCNTs solution after its surface dried in ambient air. The sample was imaged by AFM after its surface dried in ambient air again.

Due to the transparency of the film and its mica substrate beneath, the AFM tip was aligned from the film covered side with respect to the feature of the mark (an intersection of the two scratches) on the backside of the mica substrate by using the CCD and computer system (shown in Fig. 2).

After the tip alignment, an MWCNT was observed on the film surface by scanning a  $5 \times 5 \mu\text{m}^2$  large area in TappingMode AFM (shown in Fig. 3). The MWCNT was used as the mark for relocating a smaller  $1.5 \times 1.5 \mu\text{m}^2$  area.

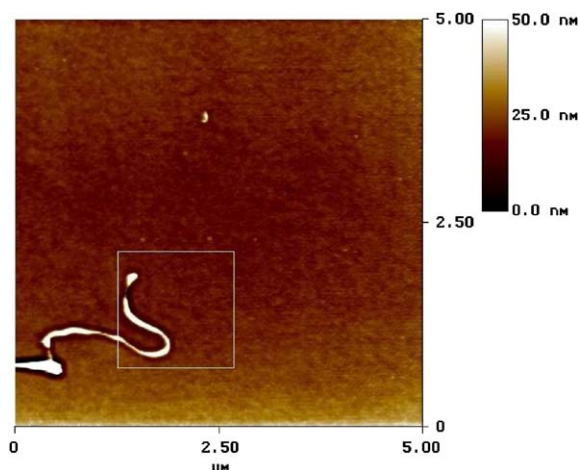


Fig. 3. TappingMode AFM image of a large-scale scan to find the small area including a MWCNT (see the area enclosed in a white square).

#### 2.4. AFM imaging

Digital Instrument multimode SPM III AFM was performed in Tapping Mode. The height and phase images were recorded simultaneously under moderate tapping conditions (set-point ratio  $r_{\text{sp}} \approx 0.70$ ) with a free amplitude of  $80 \pm 10 \text{ nm}$ , scan speed of  $1.0 \text{ Hz}$  and number of samples of  $512 \times 512$ . The operating frequency was readjusted after engaging the tip on the surface such that the operating frequency was kept on the low-frequency side of the resonance during the imaging. Commercial silicon probe tips with spring constant of about  $50 \text{ N m}^{-1}$  were used. All images were presented as only flattened raw data in order to filter the background slope.

### 3. Experimental results

Fig. 4 shows a series of time lapse AFM height images recorded at the same spot during a sequential solvent fumigating process. In the left area of all these images, the MWCNT that is responsible for relocating a  $1.5 \times 1.5 \mu\text{m}^2$  area can be seen (i.e. the area enclosed white square in Fig. 3). The microphase separation structure is clearly presented in these images. The higher domain (bright) corresponds to the PS phase while

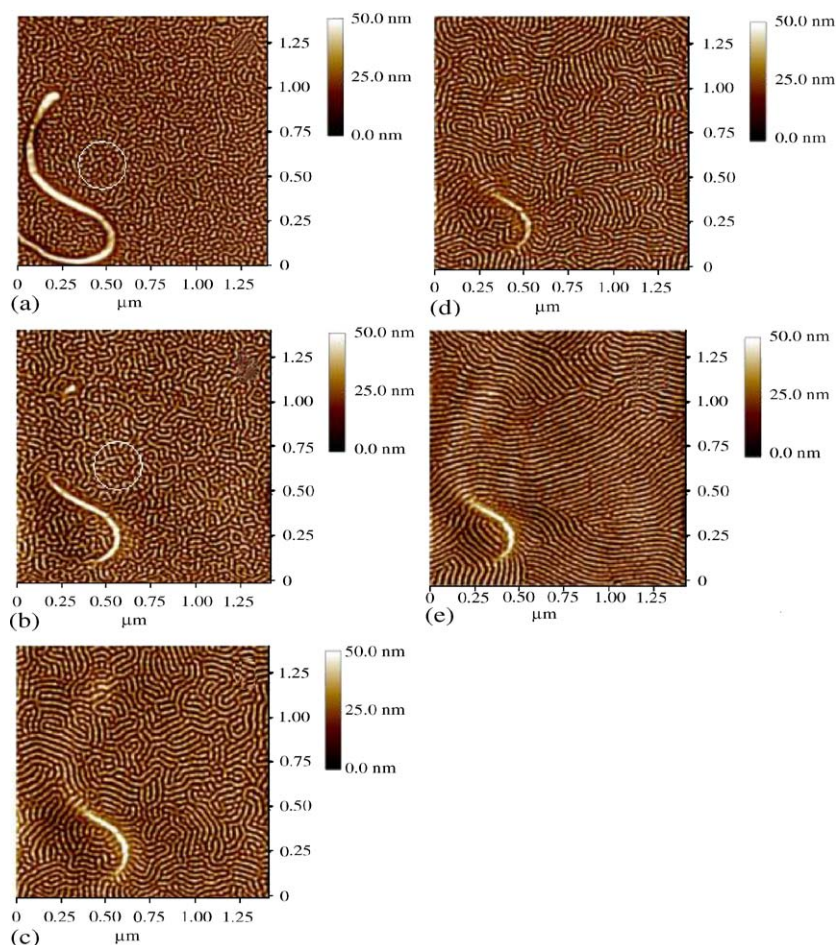


Fig. 4. A series of AFM images of block copolymer thin film recorded at the same spot before and after sequential solvent fumigating treatments: (a) as-cast, (b) 0.25 h fumigating, (c) further 0.5 h fumigating, (d) further 0.5 h fumigating and (e) further 1 h fumigating.

the lower domain (dark) corresponds to the polyethylene-butylene (PEB) phase [21,22].

Fig. 4a is the morphology of the as-cast film. The coexistence of a large number of PS cylinders, some with branches, and a small number of PS spheres in the PEB matrix can be seen on the surface. This result is in good agreement with that obtained by TEM [23].

Fig. 4b is the evolved morphology after 0.25 h solvent fumigating of the as-cast film at ambient temperature. By comparing the white circular area in Fig. 4a with that in Fig. 4b, it can be seen that the minute change in morphology evolution process was captured.

Fig. 4c–e are morphologies of further fumigating for 0.5, 0.5 and 1 h subsequently. By carefully comparing Fig. 4a–e, it can be seen that there is a dramatic change in morphology that can be categorized into two aspects: first, the PS cylinders became continuous by joining with each other. Second, partial MWCNT immersed in sample film together with continuous fumigating and scanning.

#### 4. Discussions

Using the relocating procedures, in which the repeatedly positioning scale was reduced step by



step, a more minor scanned scale relocation could be realized. A relocation precision of tens of nanometers can be reached by carefully controlling the movement of the  $x$ – $y$  translation stage. Moreover, it is worth to mentioning that unlike a previous AFM ex situ study [14,16,17] which depended on phase separation morphology clue to track the same spot, in this work, marks made on the film surface were used. The benefit of this method is that the required area will not be lost even if the morphology changes completely.

As the sample was scanned and imaged by the TappingMode AFM repeatedly, part of the MWCNT emerged in the sample film. In order to avoid the MWCNT from emerging in sample film entirely, the thickness of sample film was controlled to be less than the average diameter of MWCNTs (about 50 nm). The thickness of sample film can be measured by the method introduced in the previous report [24].

This relocating method not only has a high relocation precision, but is also efficient and easy. Therefore, it can be extensively used for the AFM ex situ study of polymer transitions and biological processes. We used a Nanoscope III system to relocate AFM samples, but the procedures outlined here could also be used for other different AFM only if it has the ability to view of backside features of the cantilever and the sample. It is noteworthy that AFM must be performed in Tapping Mode, because the sample with MWCNT will be destroyed if AFM is performed in Contact Mode.

## 5. Conclusions

Two kinds of homemade markers, crossed scratches on the backside of a mica substrate and MWCNT dispersed on the surface of the sample were used to consistently relocate the AFM tip and to perform an AFM ex situ study of morphology transition in a triblock copolymer thin film induced by xylene fumigating. The relocation method is relatively efficient, easy and reliable because it depends on the mark rather than on the changing domain pattern to be performed. A relocation accuracy of tens of nanometers can be

achieved. It is believed that this kind of simple and useful relocation method can be widely used in the field of material science and molecular biology field besides polymer.

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