Introduction

Microphase separation is a ubiquitous phenomenon in copolymer thin films due to the immiscibility and dissimilar nature of their block components. Such segregations could occur in directions both perpendicular and parallel to the underlying support substrate. In particular, the latter case will expose all of polymer components to the air/polymer interface and form periodic microdomains consisting with distinctive chemical identities. The spatial distribution (i.e., their geometry, spacing as well as patterning) of the components play an extremely important role in the chemical and physical properties of polymers.

Polymer annealing offers an effective means to tune and regulate those component domains. Generally, annealing can be introduced by heating the copolymer films well above their transition temperatures ($T_g$) to obtain enhanced microphase separations. However, such thermal annealing could induce some heating-related issues (unexpected polymer oxidation, etc.) and it fuels the research on alternative strategies such as the solvent vapor-assisted annealing. The Keysight Technologies, Inc.

7500 AFM system is comprised of a sealed environmental chamber. The desired vapor can be realized readily by putting a small vial of corresponding solution into the chamber. In this application brief, results on an atomic force microscopy (AFM)-based investigations on the annealing effect on triblock copolymer PS-b-PB-b-PS (SBS) will be presented.

AFM Structural Characterization of the Triblock Copolymer SBS without Annealing

The initial triblock copolymer SBS samples were prepared by spin-casting of their 10mg/ml solution in toluene onto a smooth silicon substrate at room temperature and under ambient conditions. Figure 1 are both AFM topography and corresponding phase images of the normal SBS copolymer without any annealing. Compositional mapping with AFM is often used for observations of microphase separation of block copolymers, which occurs at the sub-100nm scale. This is seen clearly in height and phase images of a triblock copolymer polystyrene-b-poly-
butadiene-b-polystyrene (PS-b-PB-b-PS) film. A microphase separation pattern of this material, which is mostly pronounced in the phase image, is characterized by structural parameter \( \sim 35\text{nm} \). The phase contrast is related to the fact that at room temperature, PS is in a glassy state while PB is in a rubber-like state. Consequently, the brighter areas in the phase image (corresponding higher areas in topographic image) can be attributed to stiff lamellae of PS.

### AFM Structural Characterization of the Triblock Copolymer SBS with Vapor Annealing

When block copolymer films were prepared by the spin-casting method, the resulting product and its surface morphology typically have not reached their equilibrium due to the very fast evaporation of the solvent. This is evident by the fact that those PS domains in Figure 1 are short and discontinuous. The introduction of common solvent vapor such as toluene will lead to a swelling of block copolymers. As a consequence, it could greatly facilitate the molecular motions of components and accelerate the structural evolution towards thermodynamically favored phase segregation. Such process can be monitored in real time by an AFM incorporated with a well-controlled environment. The effect the toluene vapor on the SBS structures is clearly captured by AFM. Figure 2 (left) exhibits the appearance of long-range ordering of the SBS films after a few hours. As can be seen, the in-plane cylinders become extended and formed the ordered domains as large as hundreds of nanometers. Continuous exposure to the toluene vapor allows the further changes and highly ordered domains at micrometer-scale are observed (Figure 2, right).

### Summary

Using investigations of the toluene vapor influence on copolymer SBS surface structures as an example, it is demonstrated that AFM measurements under well-controlled environments can be achieved easily with Keysight 7500 system.

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