AFM Electric Modes and Polymer Heterogeneous Materials: Blend of Polystyrene and Poly(vinyl acetate)

AFM-based electric modes such as electric force microscopy (EFM), Kelvin force microscopy (KFM) and local dielectric measurements (dC/dZ) provides selective visualization of sample components with different population of molecular dipoles, variations of surface potential and dielectric permittivity. One of the characteristic samples, which can be used for such measurements, is binary polymer blend of polystyrene and poly(vinyl acetate) – PS/PVAC. A presence of charged groups in PVAC leads to a dipole moment of 2.1 D that is much higher than that of PS. The static dielectric permittivity of the blend components are quite different: 2–3 for PS and ~7 for PVAC. In addition, the glass transition temperature - T_g of PVAC is quite low (35°C) thus its complex permittivity can also be studied with comparative ease. Furthermore, PS/PVAC can be used for local mechanical measurements as softening of PVAC above makes its elastic modulus much lower than that of PS and viscoelastic response of this component can be also explored. In addition to temperature the PVAC properties can be also changed by swelling of this polymer in methanol vapor. The sample is also useful for verification of AFM-Raman mapping with scattering in the 2920-3010 cm^{-1} and 985-1025 cm^{-1} regions suited for identification of PVAC and PS, respectively.

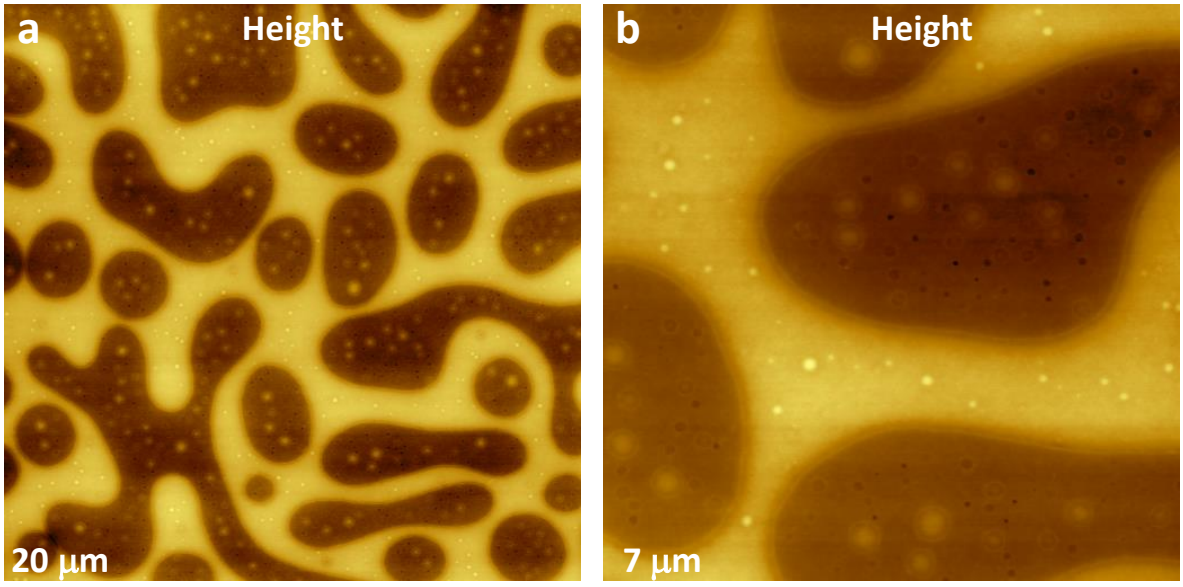

Figure 1a-b. Height images of PS/PVAC film on Si recorded in AM-PI mode with Si probe (k = 23 N/m).

Typical surface morphology of PS/PVAC blend in shown in **Figure 1a-b**. It is characterized by raised areas, which are 10 nm higher than the nearby valleys. Circular sub-micron domains, which looks like "dome" structures populate areas of both types. The film thickness is ~30 nm that will facilitate measurements of electric response. The examples of electric and mechanical studies of PS/PVAC films are different temperatures are collected in **Figures 2-4**.

Single-pass measurements of surface potential and dielectric response (see S. Magonov and J. Alexander, *Beilstein J. Nanotechnol.* **2011,** *2,* 15) of PS/PVAC film were performed on a surface location with a number of dome structures. These structures were assigned to PVAC based on the results of AFM-Raman studies and their selective swelling in methanol vapor.

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A change of the dome features in height images (**Figure 2a-b**) is also noticed as the sample temperature was increased above Tg of PVAC. This heating has influenced the surface potential contrast that became more homogeneous on PVAC locations and enhanced differences in dC/dZ map.

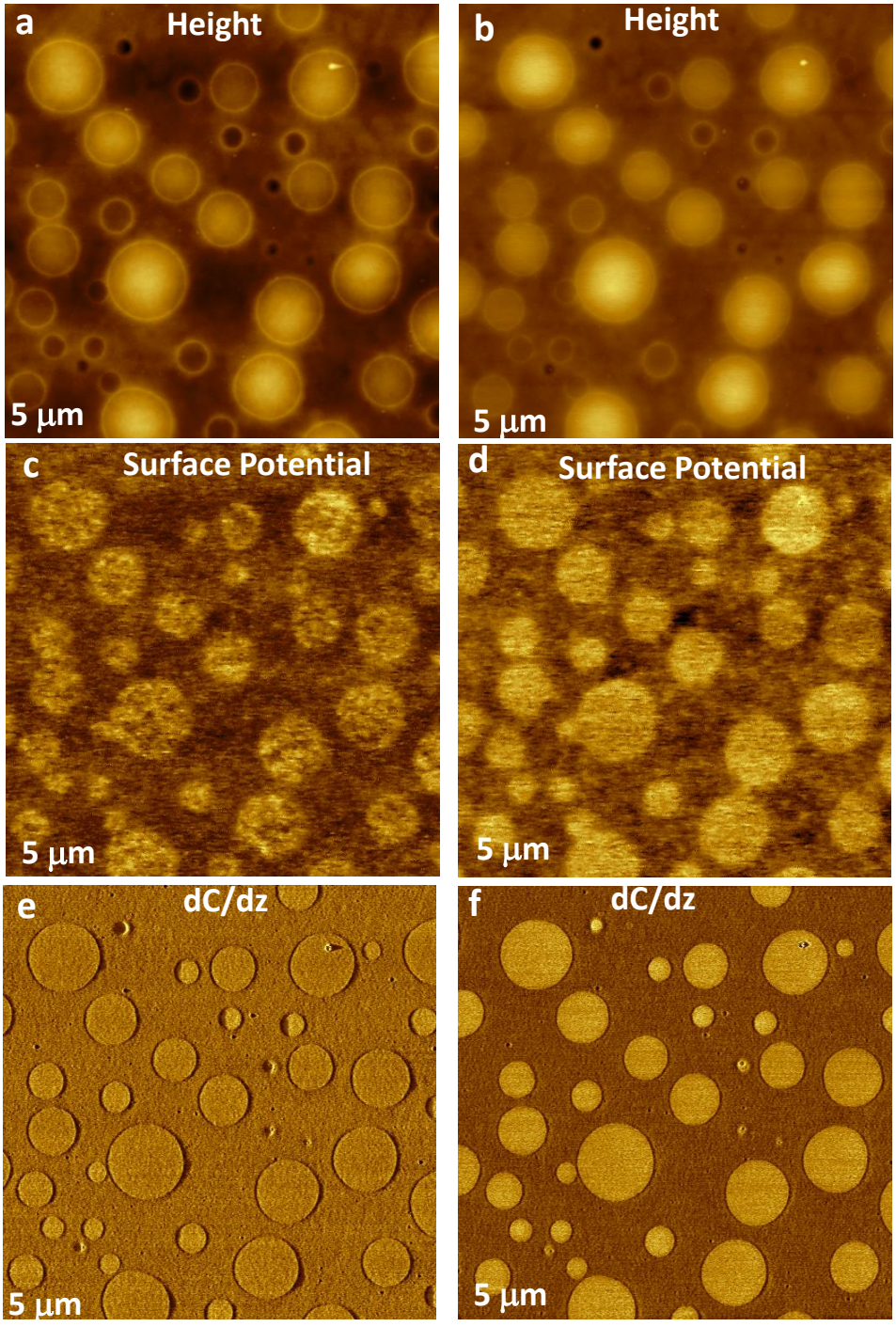

Figure 2a-f. Height images of PS/PVAC film on Si recorded in AM-PI mode with Si probe (k = 23 N/m). The images in a, c, e were obtained at 25C and the images in b, d, f – at 70C.

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It can be useful to conduct AFM imaging on areas, which include a neat substrate. This can be made by scratching a polymer film with a sharp wooden stick. The observations of such regions can be used for measurements of film thickness and getting an additional contrast due to mechanical and electric properties of the substrate. The related illustrations are given below.

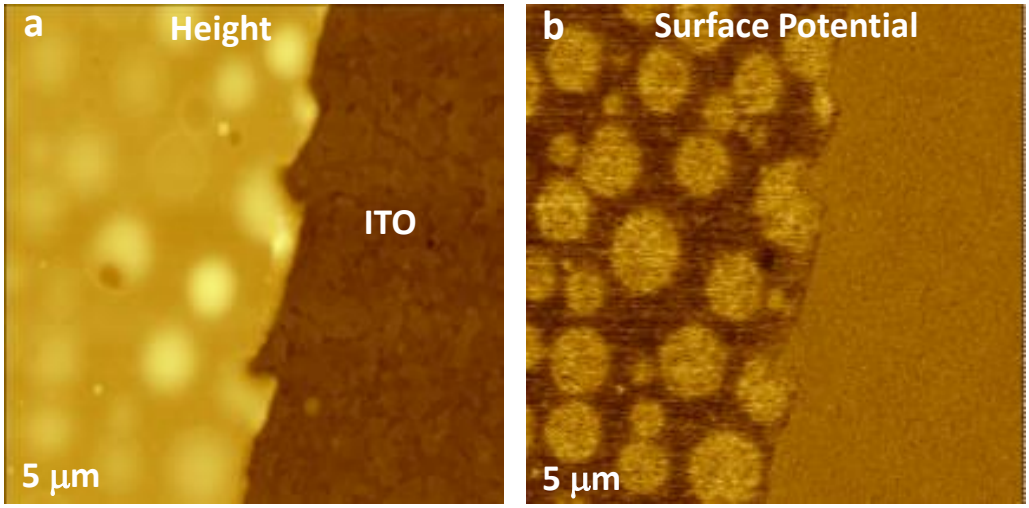

Figure 3a-b. Height and surface potential images of PS/PVAC film on ITO glass ..

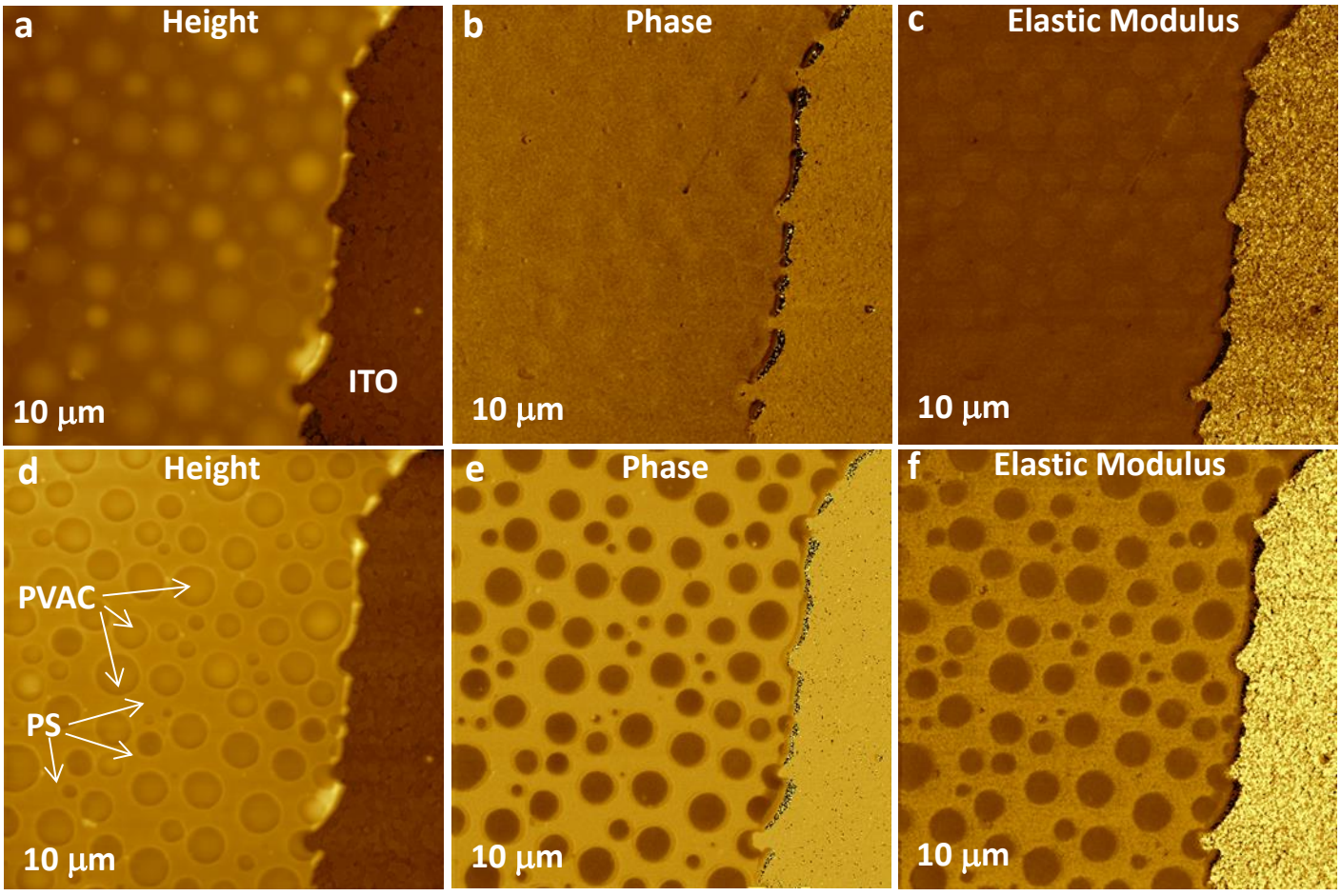

Figure 4a-f. (**a-b**, **d-e**) Height and phase images of PS/PVAC film on ITO glass . (**c, f**) Elastic modulus maps recorded in D-CNT mode. The images in (**a-c**) were recorded at 25˚C and images in (**d-f**) – at 70˚C.