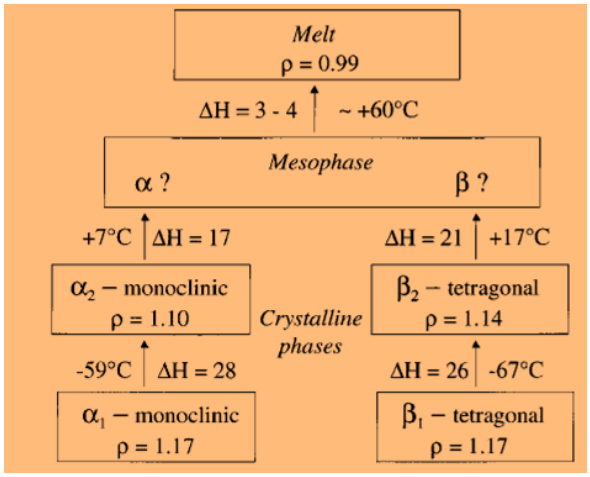
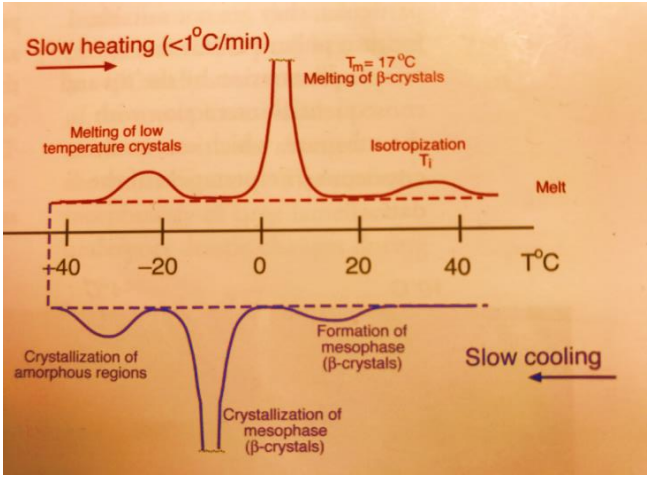
Visualization of morphology and nanostructure of polydiethylsiloxane (PDES)

PDES - Poly(diethylsiloxane) $[-Si(C_2H_5)_2-O-]_n$

Poly(di-*n*-ethyl siloxane) - PDES is non-polar flexible chain macromolecule with ethyl side groups, and this polymer exhibits a variety of crystalline and mesomorphic phases in the temperature range between -70˚C and +60˚C,





Atomic force microscopy (AFM) is helpful in characterization of the complex structure of this polymer in different states (see references below). Examination of this soft polymer in AM-PI (aka tapping) mode provides AFM images, in which the material-related phase contrast enables a distinctive visualization of crystalline, mesomorphic and amorphous components of PDES.

A common preparation of PDES sample for AFM observations is a uniaxial rubbing of the polymer on smooth substrate, e.g. Si wafer. Morphology of the rubbed sample at RT is defined by oriented strands with the substrate locations in between, **Figure 1a-b**. The cigar-like blocks represent lamellar aggregates, which are oriented perpendicular to the rubbing direction. The few dark spots in the phase image patches are amorphous PDES .

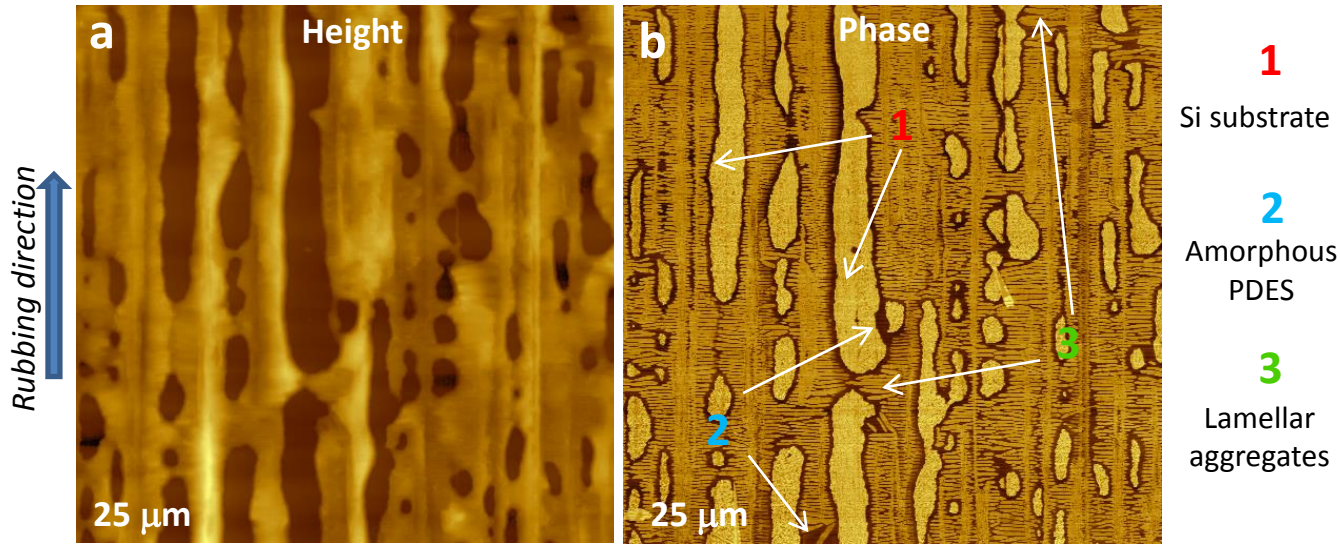


Figure 1a-b. Height and phase images of the rubbed PDES on Si substrate, which were obtained at RT.

Magonov S. N., Elings V., and Papkov V. S. "AFM Study of Thermotropic Structural Transitions of Poly(diethylsiloxane)" *Polymer* **1997**, 38, 297-307.

Godovsky Yu. K., Papkov V. S., and Magonov S. N., "Atomic force microscopy visualization of morphology changes resulting from the phase transitions in polydi-n-alkylsiloxanes: Polydiethylsiloxane" *Macromolecules* **2001**, *34*, 976-990.

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Morphology of the rubbed PDES samples at RT has similar main features but one can expect variations in local composition of the components and areas occupied by the polymer and substrate. The phase contrast also can be different for various samples and it strongly depends on a level of tip-sample force interactions defined by a probe spring constant and applied free and set-point amplitudes. These variations are illustrated by images of another rubbed sample **in Figure 2a-d**. The phase contrast in **Figure 2b** is more informative than the height image in **Figure 2a**. This is most evident from the smaller-scale images in **Figure 2c-d**. The phase image shows that the strands are composed of the comparable amounts of amorphous polymer (bright contrast) and lamellar aggregates . The substrate area in between the strands exhibits the dark phase contrast.

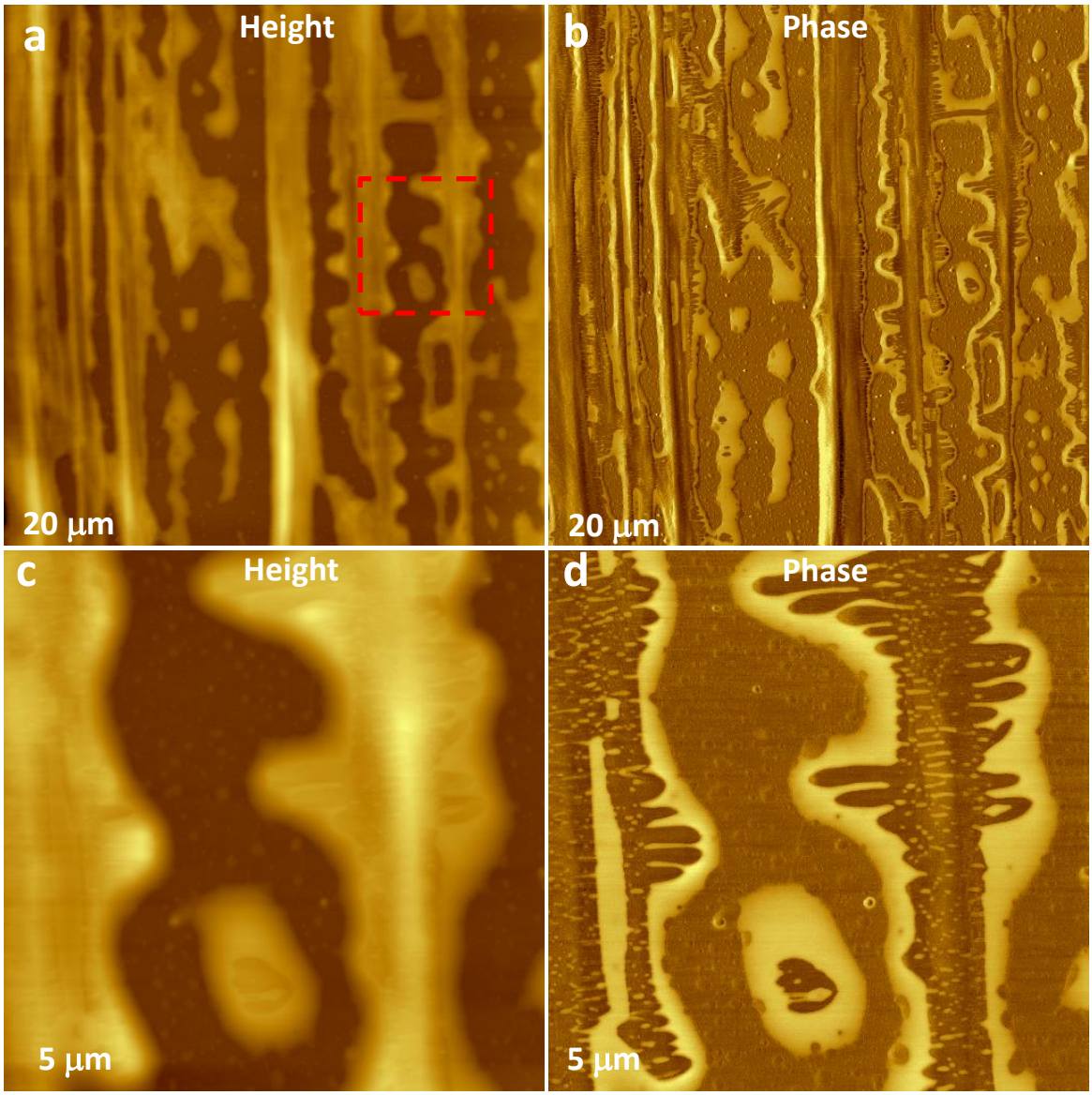

Figure 2a-d. Height and phase images of the rubbed PDES on Si substrate, which were obtained at RT. The images in (**c-d**) are taken in the area, which is marked as a dashed red square in (**a**).

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AFM monitoring of PDES structural changes at various phase transitions, is illustrated by phase images obtained at different temperatures, **Figure 3a-d**. The images were taken at the location, which is shown in **Figure 1a-b**. As temperature was raised to +38˚C, a number of amorphous PDES patches, which are identified as dark spots, has increased. At +60˚C all lamellar aggregates vanished due to the polymer isotropization. The mesomorphic state, which is associated with a formation of lamellar aggregates, has reemerged at 42˚C. This process was extended at lower temperatures, and the image at 25˚C shows a large number of new aggregates. The latter are more extended than the original ones yet they kept the same orientation.

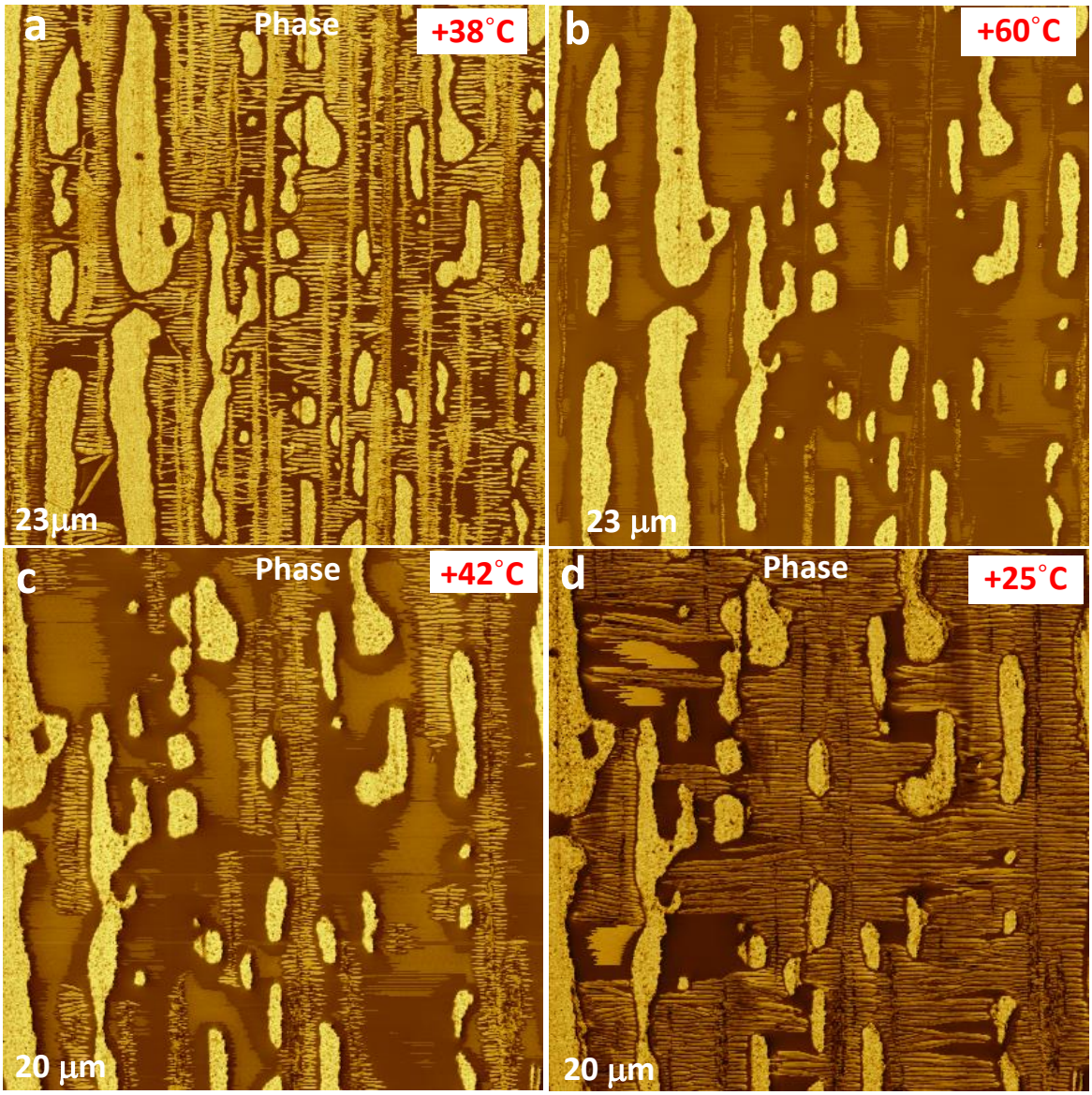

Figure 3a-d. Height and phase images of the rubbed PDES on Si substrate, which were obtained at RT. The images in (**c-d**) are taken in the area, which is marked as a dashed red square in (**a**).

Practical recommendations:

(1) Using optical control place AFM probe at substrate/polymer interface.

(2) If the rubbed PDES sample does not show the described morphology it can be rejuvenated by rubbing polymer layer e.g. with a wooden tooth-pick.