In situ GISAXS measurements on microfluidics with thermoresponsive hydrogels

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Hydrogels are chemically or physically cross-linked polymers that build-up networks in which water can be stored in large amounts, i.e. more than the volume of the polymer. In the special class of thermoresponsive hydrogels this property is linked to the temperature in a way that the amount of stored water is controlled by the temperature. Poly(N-isopropylarylamide) (PNIPAM) is a promising and frequently investigated candidate of this class. PNIPAM exhibits a lower critical solution temperature (LCST) at around 32°C and consequently the polymer can store water below this transition temperature and precipitates from water at higher temperatures as shown in fig. 1a. Thermoresponsive hydrogels with transition temperatures in the regime of the human body temperature are of particular interest because they are candidates for drug delivery systems and sensors. Studies on the thermo responsive switching of hydrogels have been popular in recent years [1]. Most studies concentrate on the behaviour of the polymer when dissolved (diluted) in water.

In our work, we are interested in thin films of PNIPAM and the swelling of these films when exposed to water. Previously this was done by investigation of the film in humid air as shown by Wang et al. [2,3]. As compared with volume samples, the thin film geometry reduces the degree of freedom to one dimension (see fig. 1b). In order to investigate the swelling not only at the presence of humid air but with pure water a micro-fluidic cell, as shown in figure 1c, is used in the presented investigation. The micro-fluidic cell is manufactured of the special material TOPAS, which is transparent to the x-ray beam in the commonly used energy range [4].

The thin film samples are prepared by spin casting from chloroform solutions onto silicon substrates. These initial dry PNIPAM films were analyzed with respect to film thickness and surface roughness. For the micro-fluidic experiment, the micro-fluidic cell is mounted on top of the thin PNIPAM film and held in place by metal clamps. Thus the use of additional glue or adhesive to fix the micro-fluidic channel on the polymer surface is avoided. Special caution has to be taken to ensure that the pressure on the substrate is equally distributed in order to prevent both, bending of the sample and leakage. The whole set-up (clamp, micro-fluidic cell and sample) was then fixed
on the hexapod stage of the new MiNaXS beamline P03 at the PETRA III storage ring. The liquid, DI water in our case, is pumped with a micro-litre pumping device that is connected via tubes to one of the inlets of the micro-fluidic cell. The second inlet (designed for mixture of liquids within the cell) is closed and another tube from the outlet leads to a basin.

The thin PNIPAM films were probed in GISAXS geometry to investigate the structure perpendicular to the sample surface while also being sensitive to changes parallel to it. In the experiments, first a measurement of the thin film without the micro-fluidic cell is carried out (see fig. 2a). Then the cell is fixed on the sample and a second GISAXS image is taken to exclude changes introduced by the mere presence of the micro-fluidic cell (see fig. 2b). Next, the surrounding polymer was removed to prove that the footprint of the beam is within the small micro-fluidic channel. The resulting 2D-image (see fig. 2c) still shows the features of the film without the cell although these features are less pronounced.

Finally, the pump was started and water moved with a speed of 0.02 ml/min into the system. Because the PNIPAM films are quite sensitive to the highly intense x-ray beam, many short measurements (exposure time only 0.5 s) with a time between subsequent measurements of 10 s were conducted, while constantly shifting the position of measurement on the sample. Therefore, the accessible time resolution was much lower than the technical limit of the beamline which limited the in situ observation of the swelling of the PNIPAM film. The film after complete exposure to the water is shown in fig. 2d. In future experiments the time resolution for this experiment will be increased with a better monitoring of the water inside the cell to finally access the time-dependent swelling of the film directly.

References

Figure 2: 2D GISAXS data in the \( q_z-q_y \)-plane at different stages of the experiment: a) before mounting of micro-fluidics cell, b) after mounting of micro-fluidics cell, c) sample outside of the micro-fluidic channel removed, d) after the water entered the channel.