Loss of interface correlation in P(S-NIPAM-S) films by means of water-based annealing

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For very smooth polymer films, spin-coated on solid substrates, a roughness correlation between the substrate and the polymer surface at the film/air interface may be observed [1], which is of particular interest because it is linked to a locally constant film thickness. In case of interface correlation, part of the roughness spectrum of the substrate is replicated by that of the upper surface of the polymer film. As a consequence, the resulting in-plane morphology of the polymer layer strongly depends on the underlying one. The smallest replicable in-plane length scale $R_c$, which is defined by the transition from a correlated to a statistically independent roughness spectrum of both film interfaces, permits to quantify the degree of interface correlation. Grazing incidence small angle X-ray scattering (GISAXS) allows evaluating the smallest replicable in-plane length scale $R_c$ for a given film. In general, roughness replication was observed for several homopolymer films. The value of $R_c$ was shown to depend on the polymer composition, on the film thickness $d$, and on thermal annealing (see [1] and ref. therein). As spin-coating typically prepares non-equilibrium film morphologies, annealing can result in a decrease or even elimination of such long-ranged correlation. For example, it was evidenced that the interface correlation vanishes during thermal annealing of a brominated polystyrene film above its glass transition temperature [1].

In the present investigation a triblock copolymer containing a block which is responsive to water is used. Correspondingly, the evolution of correlated roughness, film thickness and film morphology is investigated during the water uptake of glassy P(S-b-NIPAM-b-S) block copolymer films produced by spin-coating. As the water uptake of the initially glassy films is accompanied by a pronounced increase in molecular chain mobility, the question arises how fast the correlated roughness vanishes over time. To address these questions, the micro-fluidics setup described in reference [3] is used to ensure well defined contact between the polymer film and water. P(S-b-NIPAM-b-S) films were spin-coated on pre-cleaned glass substrates according to a basic cleaning protocol in order to achieve reproducible surface properties of the glass substrate. Using chloroform solutions of the block copolymer 56 nm thin P(S-b-NIPAM-b-S) films were prepared. All prepared films had the same film thickness and showed roughness correlation in the as-prepared state.

The GISAXS investigations using an in-situ micro-fluidics setup [3] were performed at BW4, HASYLAB at DESY, Hamburg under an incident angle $\alpha_i = 0.5^\circ$, with an X-ray wavelength $\lambda = 0.138$ nm and a sample-detector-distance of 2116 mm. In Fig. 1a the GISAXS data of a dry, as-prepared 56 nm thin P(S-NIPAM-S) film deposited on glass is shown. In case of partially or fully correlated roughness, intensity streaks of resonant diffuse scattering are expected that are oriented parallel to the $q_z$-axis [1]. This is in fact responsible for the pronounced modulation of intensity in the detector scan of the P(S-b-NIPAM-b-S) film. The spacing of these fringes $\Delta q_z = 2\pi/d_{corr}$ allows for estimating the distance between the correlated interfaces, which indeed coincides with the film thickness of 56 nm determined by X-ray reflectivity. Thus the polymer film surface is correlated with the glass surface.

During the micro-fluidics experiment, a specially designed fluidics cell [3] permits to let flow purified water over the surface of the P(S-b-NIPAM-b-S) film in a controlled way with a rate of 0.01 ml/min. The whole experiment was performed at 20 °C over 100 min. As a compromise between a high time resolution and good quality of GISAXS pictures, a data acquisition time of 10 min was selected for each GISAXS measurement during the whole fluidics experiment. In figure
2 depicts a selection of the detector cuts of the GISAXS data recorded during the fluidics experiment (see fig. 1). These cuts are obtained by summing in q_y-direction over three detector pixels (for improved statistics). Remarkably, the intensity modulation based on the resonant diffuse scattering fringes seems to be almost lost after 10 min of water uptake by the film. In the meanwhile, the film thickness has increased from 56 nm to 152 nm. During the following 90 min of the fluidics experiment, only minor changes of the detector cuts, and also of the whole GISAXS images, are observed. The film thickness slowly increases and finally amounts to 158 nm after 100 min of water uptake.

Figure 1: GISAXS data of (a) a dry, as-prepared, 56 nm thin P(S-NIPAM-S) film deposited on glass, (b) after 10 min and (c) after 100 min of water uptake. The specular peak is shielded with a point-like beamstop.

Figure 2: Selected detector cuts measured during the micro-fluidics experiment performed at 20 °C. For clarity the curves are vertically shifted with the bottom curve showing the dry initial film.

M. P. thanks the Fonds national de la Recherche (Luxembourg) for receiving a Marie Curie co-funded AFR Postdoc grant.

References