Nanophase separated poly(pentylmethacrylate-\textit{b}-methylmethacrylate)s: Structure investigations in bulk and thin films

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Nanostructured materials based on diblock copolymers possess a vigorous importance due to the opportunity to exploit their microphase/nanophase separation behaviour for developing materials with nanostructures in bulk and films or at surfaces. Because of the immiscibility of the blocks, block copolymers show self-organization and are able to form regular nanostructures on nm-length scales. The Flory-Huggins interaction parameter $\chi$, molar mass, polydispersity $M_w/M_n$ as well as the block length ratio $M_{w1}/M_{w2}$ control the phase separation in general, the type of ordered phases, as well as their thermal behaviour. In thin films, the total molar mass was recognized as important parameter determining the orientation of the nanostructure relative to the film surface.

We have continued our former investigations \cite{1} of diblock copolymers with broad variability in the chemical parameters (including a variety of functional groups) with special selected samples. One important question is to find out relationships between bulk morphology (determined mainly by molecular parameters, i.e., the block ratio, molar mass, thermal history), and morphologies in thin films, which are strongly influenced by film parameters and film thickness related to bulk domain spacings. PPMA-\textit{b}-PMMA diblock copolymers with predominantly hexagonally close-packed cylinders in the bulk and varied molar masses but identical molar composition were chosen for examination (synthesis via sequential living anionic polymerization in THF allows to prepare samples with low polydispersities $M_w/M_n \sim 1.1$). Thin films with thicknesses below and above the bulk domain spacing were prepared on Si(111) wafers by dip-coating from polymer solutions (1 or 2 wt\% in THF) at room temperature with different withdrawal speeds. Additionally, the experimentally found phase behaviour of the diblock copolymers was compared with the calculated phase diagram.

One aim of this work was to clarify and compare the phase behaviour of PPMA-\textit{b}-PMMA in bulk and thin films (with T-SAXS at beamline A2 and GIXS at beamline BW4). To analyse the morphology in confined dimensions, thin films were prepared with two different film thicknesses $f$, smaller and slightly bigger than the bulk domain spacings $d_{\text{bulk}}$. In thin films with $f < d_{\text{bulk}}$, lying (parallel) morphologies are expected to be suppressed due to confinement effects \cite{2}. The phase behaviour in thin films was detected by AFM, additionally.

The systematic search for laterally ordered and demixed morphologies is an essential pre-condition to obtain surfaces with regions of different properties, which can serve as template for selective tethering of different species (e.g., nanoparticles) \cite{3}. In all cases, the dip-coated thin films formed nanostructured surfaces. Mostly, the periodicities of nanostructures in thin films were comparable to the periodicities obtained in bulk samples. Occasionally, the bulk structure has been partly modified in thin films. The arrangements of cylinders (standing or lying) were governed by the film thickness dependent on the molar mass of the block copolymer. Vertically standing cylinders were formed for film thicknesses $f$ smaller than $d_{\text{bulk}}$ only in the case of the sample with higher molar mass. Significantly thicker films ($f \gg d$) were not suited for laterally structured surfaces with desired pattern in this class of diblock copolymers. An open question is whether or not the films obtained by dip-coating and post-annealing are in thermodynamic equilibrium. This has to be clarified in future investigations.

For illustration of the results of several samples see Figure 1 and 2 \cite{4}.
Figure 1: Temperature-dependent SAXS curves of a 67/33 mol/mol as-synthesized sample - first heating/cooling run with 3 K/min. At T ~ T_g(PMMA) an hcp cylinder morphology is generated (a_hex = 48.4 nm). Reflection assignment: 1 - d_(100), 2 - d_(110), 3 - d_(200), 4 - d_(210), 5 - d_(300), 6 - d_(220). The corresponding reflection ratios are 1 : \sqrt{3} : 2 : \sqrt{7} : 3 : \sqrt{12}.

Figure 2: 2D-GISAXS pattern of a) ~25 nm film consisting of standing PMMA cylinders (hcp in extended areas) (normal to the surface); b) ~50 nm film consisting of short lying bent PMMA cylinders (parallel to each other in limited areas). Lateral correlation peaks assigned by arrows. For illustration see pictograms. Corresponding AFM images are in between (phase contrast, 1×1 µm²).

References


