Imprint strategies for directed self-assembly of block copolymers

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Typically, directed self-assembly (DSA) of block-copolymers (BCP) is provided by grapho-epitaxy or chemo-epitaxy [1], where each single substrate has to be pre-patterned either with a topography or with a chemical nano-pattern prior to BCP application and DSA. When lamellar BCPs are addressed [2] often a chemically 'neutral' surface is asked [3] which is easiest obtained by grafting of a random copolymer that fits to the block ratio of the respective BCP [4]. Unfortunately this approach is impaired by the fact that such random copolymers for grafting are not commercially available.

A highly attractive alternative would be to induce DSA in an inverted direction, from the top of a BCP layer to the bottom, and thus to overcome the laborious pre-patterning of each single substrate. When such an approach to DSA is induced by a mould, this mould is re-usable many times, thus reducing the overall effort significantly. Then, with respect to realization, nanoimprint methods are addressed.

Such an approach is challenging. With nanoimprint the 'boundary conditions' differ substantially from those with classical DSA methods. The ordinary control parameter with grapho- and chemo-epitaxy, the surface energy, is largely prohibited as the stamp requires an anti-sticking layer. However, during imprint the polymer is squeezed into the cavities imposing dynamic conditions instead. Fig. 1 indicates potential DSA situations within a stamp cavity. With a certain height $H$ of the stamp the choice of the initial polymer thickness $h_0$ controls the residual layer height $h$, and thus the BCP height within the cavities $h_{cav}$. When $h_{cav}$ is not commensurate with the lamellar period $L_0$ a vertical orientation of the lamella within the cavities seems to be achievable, despite the inherently preferential surface energy of stamp and substrate, as sketched in Fig. 1 c,d. Obviously this approach seems to work. Fig. 2 shows PS-b-PMMA lamella oriented parallel to the stamp cavities, perpendicular to the squeeze direction. In order to minimize any pre-assembly during heat-up of the imprint system the imprint stack was loaded afterwards. The imprint situation was similar to Fig. 1 d, however, a negligible residual layer was not yet obtained. Therefore we investigated the imprint-ability of the BCP (see caption of Fig. 3). With a higher imprint temperature the residual layer can be sufficiently reduced, so that $h$ drops below $L_0 / 2$. Fig. 4 presents a result with a negligible residual layer. The stamp cavities were not filled completely and the surface of the imprinted line looks quite smooth. After VUV-treatment and PMMA removal the surface is washed out and features distinct undulations along the cavity, indicating a pre-separation of the BCP induced by the imprint.

We will exploit this imprint-induced pre-separation in a two-step process. As indicated in Fig. 5 the sample is loaded after heat-up, the imprint is performed at a high temperature to minimize the residual layer and to induce pre-separation and finally the BCP is allowed to improve its self-assembly at a sufficiently low temperature to induce efficient phase separation. To adjust convenient imprint situations for vertical phase separation along the cavities we will use stamps of adequate height.

Imprint at a pressure of 100 bar, imprint time 1h at 150°C. The imprint machine was not loaded with the imprint stack until the heat-up was completed. To visualize the DSA the PMMA was damaged by VUV-treatment and removed in acetic acid.

The data points for the BCP were obtained by comparing imprint results of the BCP and of PS that has been characterized rheologically. (Curves are fitted according to the WLF equation.)

The imprint is performed at a high temperature to achieve a high imprint depth (negligibly thin residual layer). In a second step the BCP is annealed at a lower temperature for DSA along the cavities.