Structure investigations in thin films of poly(pentyl methacrylate-*b*-methyl methacrylate)s and their nanocomposites with nanoparticles

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Diblock copolymers with low polydispersity form nanostructured materials owing to micro/nanophase separation in bulk which can also generated in thin films and at surfaces. The structure in thin films is only understandable if basic information about the bulk morphology is available. In thin films, additionally, preferential forces (for instance surface forces) have to be taken into account altering the morphology in confined dimensions often drastically. As consequence, the orientation of the morphology depends on the thickness of the thin film. Cylinder or lamellae structures may be formed which are aligned parallel (lying) or perpendicularly (standing) relative to the film surface. We found in former investigations of cylindrical PPMA/PMMA block copolymers that the molar mass determined the bulk d-spacing (periodicity) d_{bulk}. If the film thickness in thin films was well below d_{bulk}, standing cylinder morphologies were observed, while film thicknesses around and larger d_{bulk} resulted in parallel-arranged lying cylinders. The results for lamellar PPMA/PMMA were more complex and often did not indicate defined and reproducible morphologies. Thus, we continued here with cylindrical block copolymers and aimed on two topics: 1) will vapour annealing allow altering/improving the morphology, and 2) would incorporation of nanoparticles (silica, gold, silver) change the morphology of this special all-methacrylic block copolymer system significantly.

We continued our former investigations [1-3] of PPMA/PMMA diblock copolymers with known morphology [4], in particular focused on PPMA/PMMA with molar composition of 70/30 mol/mol generating cylindrical structures (hexagonally close-packed PMMA cylinders in the PPMA matrix, as proven by T-SAXS experiments on powdered samples at A2 beamline). The block copolymers were synthesized by living anionic polymerization in THF at -78 °C using *sec*-butyl lithium / diphenyl ethylene as initiator.

These block copolymers were filled with different types and amounts of nanoparticles (SiO_x, metallic nanoparticles) mainly by dissolving the samples in THF, adding either the precursor or the nanoparticles followed by the standard dip-coating procedure as used for the pure BCP films.

The morphology in thin films was imaged AFM in height and phase contrast to have a first impression and support in interpretation the GISAXS results.

GISAXS experiments were performed at constant (and optimized) incident angle (below the critical angle α_c of the film material). By using of a special vapour cell (from the TUM's group "Physics of soft matter" [2]) series of measurements under constant scattering conditions were done in dependence of a constant solvent vapour flow ("vapour annealing", first) and a nitrogen flow ("drying", second). Different solvents (THF, chloroform) were tested.

For a first chosen sample set (film thicknesses below the bulk dimensions of morphology), standing cylinders or a mix of standing and lying structures was detected in all samples. In the case of the pure diblock copolymer film, the same morphology as in solid state was generated. In nanocomposites, the type of the morphology remains the same, but the dimensions were changed depending on the type and amount of incorporated nanoparticles. As a common result, it was found that SiO_x clusters enlarge the lateral distance of the cylinders, whereas metallic nanoparticles often rather reduce this parameter. The effect of "vapour annealing" is weak under the conditions chosen so far. In general, the quality of the morphology was slightly improved and the lateral distances kept

constant or were reduced a little. The expected significant switching of morphology orientation upon vapour annealing could not be detected yet (further experiments necessary). Thus, next experiments will be directed to investigation of defined thicker films and/or applying of other solvents.

For illustration of results, see Figure 1a-d.

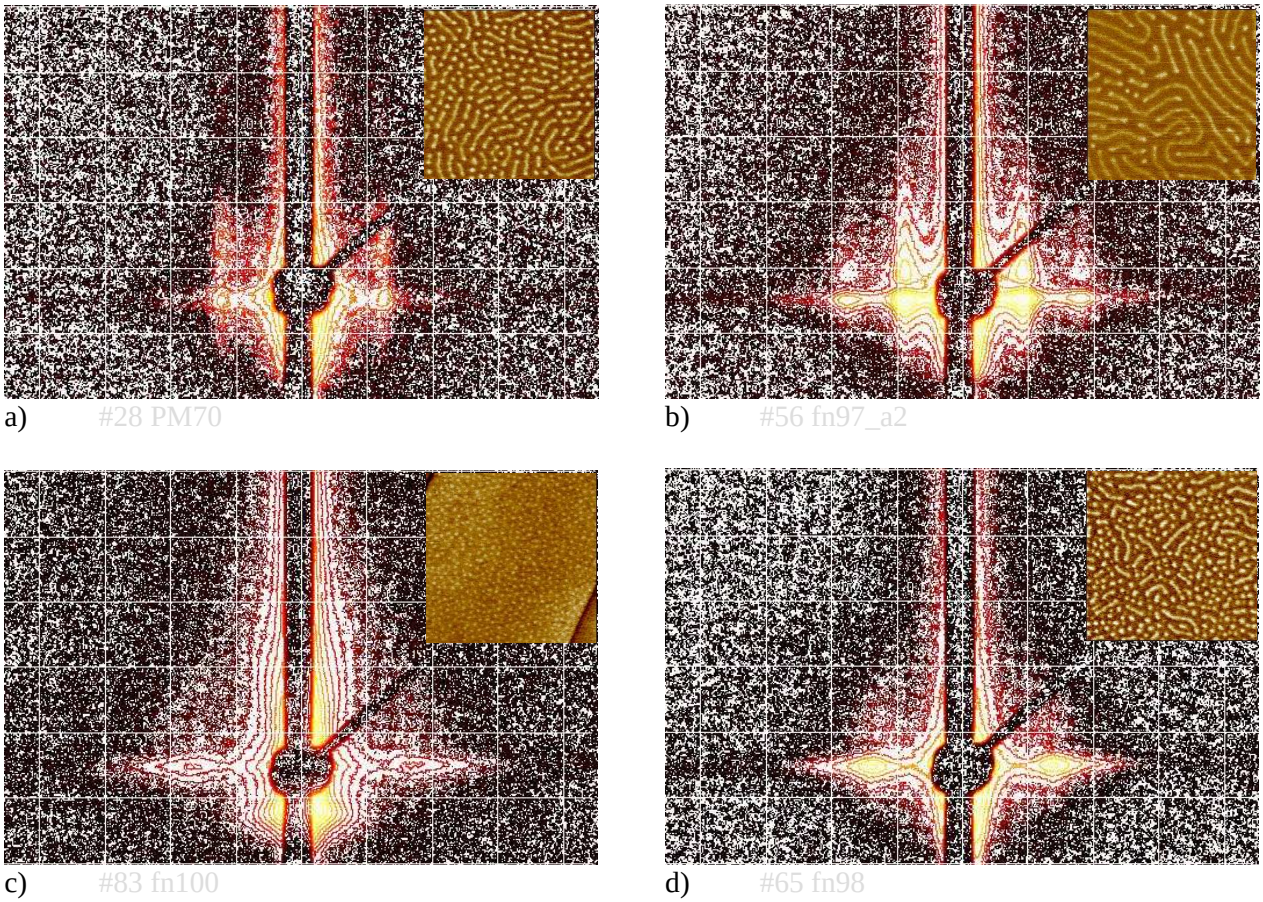

Figure 1: 2D-GISAXS pattern of ~35 nm films consisting of standing PMMA cylinders (hcp in extended areas) in a PPMA matrix (normal to the surface) with nanoparticles; a) pure basic block copolymer PM70 (PPMA/PMMA 70/30), b) PM70 with 3.3 wt-% SiO_x, c) PM70 with 0.3 wt-% Ag, d) PM70 with 0.7 wt-% Au. Scattering patterns are overlapped by a (not neglectable) amount of lying structures (PMMA cylinders). Inserts: corresponding 1×1 μm^2 phase contrast AFM images.

References

[1] D. Jehnichen, D. Pospiech, S. Ptacek, K. Eckstein, P. Friedel, A. Janke, A. Korwitz, C.M. Papadakis, A. Timmann, and S.S. Funari, HASYLAB Annual Report 2007, DESY Hamburg (2008), Part I, 1369 & D. Jehnichen, D. Pospiech, S. Ptacek, P. Friedel, A. Korwitz, C.M. Papadakis, and S.S. Funari, HASYLAB Annual Report 2009, DESY Hamburg (2010), 2009418.pdf.

[2] D. Jehnichen, D. Pospiech, R. Kęska, S. Ptacek, A. Janke, S.S. Funari, A. Timmann, and C.M. Papadakis, *J. Nanostructured Polymers and Nanocomposites* **4**, 119-128 (2008)

[3] D. Jehnichen, D. Pospiech, S. Ptacek, K. Eckstein, P. Friedel, A. Janke, and C.M. Papadakis, *Z. Kristallogr. Suppl.* **30**, 485-490 (2009).

[4] S. Werner (Ptacek), D. Pospiech, D. Jehnichen, K. Eckstein, H. Komber, P. Friedel, A. Janke, F. Näther, U. Reuter, B. Voit, R. Taurino, and M. Messori, *J. Polym. Sci., Part A: Polym. Chem.* **49**, 926-937 (2011).

[5] F. Näther, „Gezielte Anordnung von Nanopartikeln mit Hilfe von Blockcopolymertemplaten: Herstellung und Eigenschaften von Blockcopolymerhybriden“, MSc Thesis, HTW Dresden, 2010.