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Tunable morphologies in charged pentablock terpolymers in thin film geometry: effect of solvent vapor annealing

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Self-assembled morphologies of thin films of a pentablock terpolymer with a symmetric architecture of two types of pH-responsive midblocks and short hydrophobic end blocks are investigated. Different degrees of charge, installed for the two pH-responsive blocks by varying the pH-value of the aqueous solution used for spin-coating, strongly define the film formation behaviour [1]. However, with the high glass transition temperatures of the middle pH-responsive block and the hydrophobic end blocks, the as-prepared films are not necessarily in equilibrium. Here, we investigate further accessible morphologies by swelling the films in the vapors of solvents having different selectivity. In situ grazing-incidence small-angle X-ray scattering (GISAXS) suggests that water vapour (exclusively swelling the pH-responsive blocks) disorders the film in the swollen state, while it leaves the nanodomains rather intact after drying. Methanol vapor (swelling all blocks), in contrast, enhances microphase separation, and the film stays ordered at all stages of SVA. Restructurization, in general, was found to be more pronounced at higher pH-values, where both pH-responsive blocks are uncharged.

[1] F. A. Jung, M. Schart, L. Bührend, E. Meidinger, J.-J. Kang, B.-J. Niebuur, S. Ariaee, D. S. Molodenskiy, D. Posselt, H. Amenitsch, C. Tsitsilianis, and C. M. Papadakis, *Adv. Funct. Mater.* 31, 2102905 (2021).

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