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Vapor Treatment of Block Copolymer Thin Films: GISAXS and Simulations

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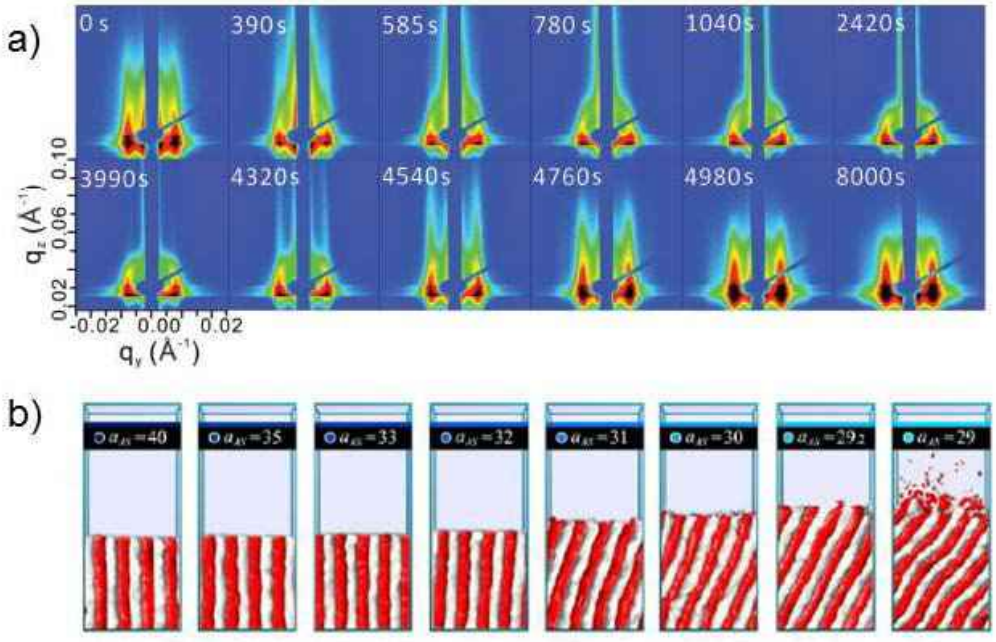
The structural evolution in poly(styrene-b-butadiene) (P(S-b-B)) diblock copolymer thin films during treatment with cyclohexane vapor is investigated in-situ and in real-time using grazing-incidence small-angle X-ray scattering (GISAXS) [1]. Both the swelling and the drying process are investigated. The lamellae are initially perpendicular to the film surface, i.e. the film is laterally nanostructured. Cyclohexane is a good solvent for PB and a theta solvent for PS, i.e., it is slightly selective. Using incident angles above and below the polymer critical angle, structural changes near the film surface and in the entire film are distinguished. We find that, during swelling, the initially perpendicular lamellae tilt within the film. Our computer simulations [2] show that this is due to the tendency of the copolymers to assume less stretched chain conformations, i.e. the lamellae shrink upon solvent uptake. Since long-range mass transport is not easily possible, tilting allows satisfying the space-filling condition when the lamellae are shrinking. Surface-sensitive GISAXS experiments show that, at the film surface, the lamellae eventually vanish at the expense of a thin PB wetting layer. During the subsequent drying, the perpendicular lamellae reappear at the surface, and finally, PS blocks protrude because of the solvent selectivity. By modeling the 2D GISAXS images, the time-dependent height of the protrusions can be quantitatively extracted. Figure 1. (a) 2D GISAXS images during swelling (top row) and drying (bottom row). The times after the beginning of the vapor treatment are indicated. (b) Snapshots from computer simulations of perpendicular lamellae which tilt during the film swelling. From left to right, the degree of swelling increases.

[1] *J. Zhang, D. Posselt, A. Sepe, et al., Macromol. Rapid Commun. 2013, 34, 1289-1295.,* ***[2]*** *A.A. Rudov, E.S. Patyukova, I.V. Neratova, et al., Macromolecules 2013, 46, 5786-5795.*



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