Structural changes in thin block copolymer films during vapor treatment

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Vapor treatment is a powerful alternative to thermal annealing of block copolymer thin films. It is routinely used to anneal defects and to improve the long-range order. However, the processes going on during structural rearrangements are complex: The solvent increases the chain mobility and reduces the effective Flory-Huggins interaction parameter between the blocks [1]. The latter results in a tendency to more coiled block conformations with a higher interfacial demand per block and, finally, to disordering.

We have investigated thin films of poly(styrene-b-butadiene) during vapor treatment. Both toluene, a good and non-selective solvent [2] and cyclohexane, a slightly selective solvent [3] were chosen. The samples were exposed to saturated vapor. To investigate the structural changes in-situ, we carried out grazing-incidence small-angle x-ray scattering with a time resolution of a few sec.

In both cases, a transient state with an overshoot of the lamellar thickness is observed which we attribute to uniaxial swelling before the glass transition of polystyrene is reached. Once the glass transition is crossed, the chain mobility increases and new lamellae can be formed which allows the blocks to assume more coiled chain conformations. Eventually, the solvent content in the film is so high that the disordered state is reached.

![GISAXS image during swelling with toluene vapor (left) and suggested intermediate state together with swollen state (right).](image)