GISAXS on photocleavable PS-*b*-PEO nanoporous thin films

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The utilization of the bottom up approach to fabricate regular arrays of nanostructures patterning from block copolymer will open the possibility to use this patterning in a system such as a polymeric membrane or a template for nanostructure materials. Thus, exploring the quantum efficiency of photocleavage and the diffusive transport of the cleaved domain out of the system are of strategic importance of meeting these future applications. Upon the UV irradiation, the photocleavable part in a highly ordered PS-b-PEO thin film will be removed out of the system by choosing an appropriate solvent leaving a nanoscopically-patterned. Thereby, it is important to figure out the best washing solvent and the best washing time for the selective degradation of the core material. In favor of this, the surface morphology of block copolymer thin films was measured using Grazing-Incidence Small Angle X-Ray Scattering (GISAXS) technique.

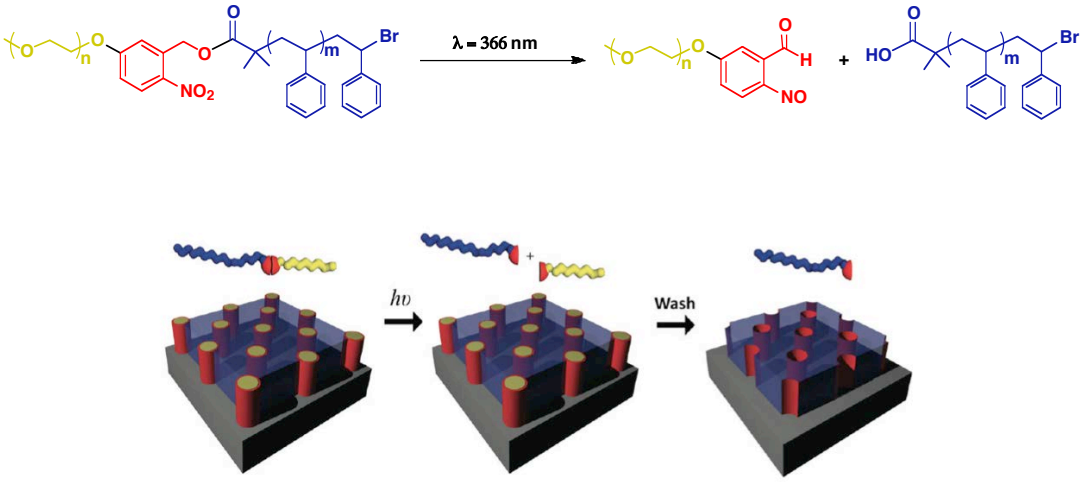
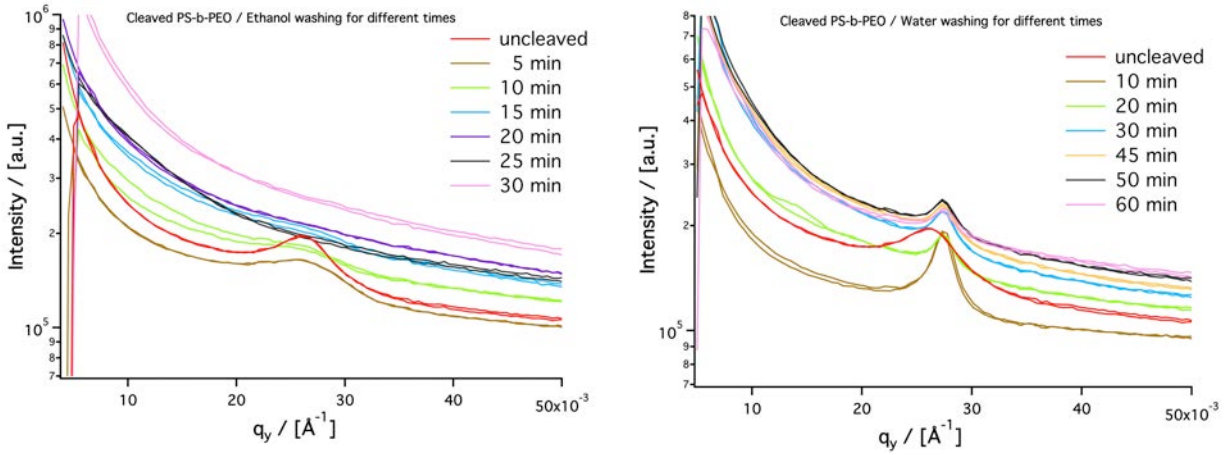


Figure **1**: Schematic representation of the self-assembly of photocleavable block copolymers and the subsequent removal of one domain upon photo cleavage and washing.

The GISAXS measurements were investigated at the P03 beamline with a beam size of 28x22 μm^2 (horizontal x vertical) and a wavelength of λ = 0,1088 nm. The sample-to-detector distance was around 2m. For the polymer thin films we utilized an angle of incident α_i = 0.4°. By GISAXS we proposed to identify a suitable washing protocol as

studying a 5 time steps on a single sample for both washing solvents ethanol and ultra pure water. For each time step approximately the whole sample surface (2 cm x 2 cm) was scanned by stepwise moving the sample stage in the lateral direction. For the analysis the images of these scans were summed up into one image to increase the scattering intensity. In order to detect the formation of nanodomains of the photocleaved polymer film, we implemented the out-of-plane scan cuts on the 2D GISAXS patterns to demonstrate the 1D scattering profiles as shown in figure 2.



a) Ethanol washing for different times

b) Water washing for different times

Figure **2**: Out-of-plane cut of the 2D–GISAXS images of the photocleaved block copolymer films washed with ethanol (a) and water (b) at different time.

The GISAXS data clearly show the self-assembly of the used copolymer film as well as the generation of nanoporous domains after washing. On the other hand, data also show that even for short washing time the scattering peak disappears (for ethanol) or the peak intensity decreases with slightly shift of the peak position (for water). Furthermore, we can conclude that the distance between two domains calculated for q_y at peak maximum is 23-24 nm in good agreement with that determined using AFM technique. The evidence is that after treatment the high orientation gets destroyed because a swelling process on the film occurs.

References

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