Supporting information: readily available titania nanostructuring routines based on mobility and polarity controlled phase separation of an amphiphilic diblock copolymer

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Influence of Evaporation Time (exceeding 100 s) on Phase Separation Behavior:

To analyze the inner morphology of films with titania nanostructures for evaporation times exceeding 100 s GISAXS measurements are performed. The same procedure, as done for shorter evaporation time studies, is carried out. Corresponding horizontal line cuts from the 2D GISAXS data are shown in Figure S1. Similar to evaporation times from 1 s to 100 s a shoulder like peak can be observed indicating the formation of a porous nanostructure. Nevertheless, there appears to be no further dependence on a change of evaporation time. As represented by the black dotted arrow the peak positions remain almost constant for longer times.

Quantification is achieved via fitting of the horizontal line cuts with the same model as applied for shorter evaporation times. The extracted sizes and distances of titania nanostructures are shown in Figure S2. Obtained sizes are found around 6 nm, while distances are found around 22 nm. With increasing evaporation, no significant change is seen within the range of the errors.

Consequently, it is assumed that the sample is already in a dry state meaning that the good solvent, in this case the toluene, is already completely evaporated. Therefore, no dependence could be found for a further increase of the discussed influence.

2D GISAXS data of Influence of Poor Solvent Composition on Phase Separation Behavior

Figure S1. Horizontal line cuts of 2D GISAXS data at the material specific Yoneda peak position after different evaporation times. As indicated by the dotted arrows no shift of the shoulder-like feature is visible for different evaporation times. Data points left to the dashed line originate from the laterally extended Yoneda region, the so-called resolution regime. The resolution limit is shown by the vertical dashed line. Data and fits are shifted along the y axis for clarity of the presentation.
Shown in Figure S3 are the 2D GISAXS images for different solvent bath compositions, which have been measured at the MINAXS beamline P03 at DESY. Referring to Figure S3a only weak lateral scattering is detected. With increasing the 1-butanol content the overall scattering is increasing (Figure S3b/c), while Bragg rods are as well starting to become more prominent. Since the formation of these rods is related to the formation of a periodic structure, an increase in 1-butanol is evidently beneficial to enhance the structuring process of titania. Exceeding 1-butanol concentrations of 40 vol% the lateral intensity peak becomes less pronounced and appears to have an increased FWHM. This observation is best seen when comparing Figure S3d with Figure S3i. Accordingly, the lateral peak at the \( q_z \) position of the Yoneda peak is easily visible for 40 vol%, while it is more difficult to identify a change of intensity along the same direction for 90 vol% from simply looking at the 2D GISAXS data. This increase in disorder is as well confirmed in SEM images and is attributed to the decreased content of good solvent. Finally, it can be stated that the most periodic structure is expected for 1-butanol concentration in between 30 vol% and 40 vol%.

**Porosity and Film Thickness**

To confirm that the \( q_z \) shift of the Yoneda peak position relative to an expected value for compact titania is indeed related to the presence of a completely porous titania layer, cross section SEM measurements have as well been performed. An exemplary image for 90 vol% 1-butanol in the immersion bath is depicted in Figure S4 which confirms the conclusions drawn from the GISAXS measurements. Note that cross section SEM images have been taken for every sample and no significant changes between surface and bulk morphologies are found for evaporation times \(< 100 \) s. Furthermore, for the evaporation time series an approximately constant thickness of 170 nm is confirmed via profilometry measurements (Figure S5).

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**Figure S3.** 2D GISAXS data for different compositions of the immersion bath (as indicated in the insets). From top to bottom and left to right the 1-butanol content is successively increased. In (a) only weak lateral scattering is detected. With increasing the polarity, the lateral structures become more prominent and distinct. In (c) and (d) a maximum lateral scattering is reached, which decreases and smears out again with 1-butanol contents above 50 vol%. All data are shown with the same intensity scale bare is indicated.

**Figure S4.** Exemplary cross section SEM of a porous titania layer synthesized via immersion into a 90 vol% 1-butanol solvent bath. Clearly visible is that the whole film consists of porous titania and no significant differences are observed between surface and bulk morphology.

**Figure S5.** Thickness estimation via profilometry for different evaporation times of mesoporous titania layers. Note that for every film 3 scratches (center, edge and intermediate position) with 5 lines have been measured.