Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supplemental Information:

Self-Assembly Morphology of Block Copolymers in Sub-10 nm Topographical Guiding Patterns

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Additional information about derivation of e_D

This part of the document is to provide additional insight into the determination of the parameter e_D.

The free energy of

$$\frac{e_T}{e_0} = \frac{1}{3}\left(\left(\frac{p}{n*L_0}\right)^2 + \frac{2*n*L_0}{p} + \frac{2*\Gamma*L_0}{p}\right) \qquad \text{(S1)}$$

can also be written as

$$\frac{e_T}{e_0} = \frac{e_0+e_{S,\lambda}+e_{AB,\lambda}+e_{AW}}{e_0} \qquad \text{(S2),}$$

where e_0 is the bulk free energy, $e_{s,\lambda}$ is the free energy penalty induced due to the chain deformation from the minimum free energy chain length $^{L}0/_{2}$. Furthermore, $e_{AB,\lambda}$ is the free energy contribution due to the change in A/B-interfaces upon domain deformation. The term e_{AW} is the free energy contribution due to the polymer-wall interaction.

Accordingly,

$$\frac{e_{Tt}}{e_0} = \frac{1}{3}\left(\left(\frac{p}{n*L_0}\right)^2 + \frac{2*n*L_0}{p} + \frac{2*\Gamma*L_0}{p}\right) + \frac{e_D}{e_0} \qquad \text{(S3)}$$

can also be written as

$$\frac{e_{Tt}}{e_0} = \frac{e_0+e_{S,\lambda}+e_{AB,\lambda}+e_{AW}}{e_0} + \frac{e_D}{e_0} \qquad \text{(S4)}$$

On the other hand, we know that

$$\frac{e}{e_0} = 1 + \frac{e_{AW}}{e_0} + \frac{e_P}{e_0} \qquad \text{(S5)}$$

Using equations *(S2)* and *(S5)*, we can state

$$\frac{\Delta e}{e_0} = \frac{e_T}{e_0} - \frac{e}{e_0} = \frac{e_{S,\lambda}+e_{AB,\lambda}}{e_0} - \frac{e_P}{e_0} \qquad \text{(S6)}$$

In a previous work[1], we have determined

$$\frac{e_P}{e_0} = 0.007 \qquad \text{(S7)}$$

On the other hand, using the equations *(S4)* and *(S6)*, we can state accordingly:

$$\frac{\Delta e_t}{e_0} = \frac{e_{Tt}}{e_0} - \frac{e}{e_0} = \left(\frac{e_{S,\lambda}+e_{AB,\lambda}}{e_0} + \frac{e_D}{e_0}\right) - \frac{e_P}{e_0} = \frac{e_{S,\lambda}+e_{AB,\lambda}}{e_0} - \left(\frac{e_P}{e_0} - \frac{e_D}{e_0}\right) \qquad \text{(S8)}$$

Now, fitting our experimental results (i.e. defects in 80 nm and 110 nm pattern, and defect-free alignment in 90 nm and 120 nm pattern) to determine the offset $(\frac{e_P}{e_0} - \frac{e_D}{e_0})$ yields

$$\left(\frac{e_P}{e_0}-\frac{e_D}{e_0}\right)=0.004 \qquad \text{(S9)}$$

In the case that the chains are not deformed at all (i.e. $e_{s,\lambda} = 0$ and $e_{AB,\lambda} = 0$),

$$\frac{\Delta e_t}{e_0}=\left(\frac{e_P}{e_0}-\frac{e_D}{e_0}\right) \qquad \text{(S10),}$$

which means that $\left(\frac{e_P}{e_0}-\frac{e_D}{e_0}\right)$ equals the maximum energy difference between the defect-loaded and the defect-free state in the directed self-assembly of block copolymers in topographical guiding patterns in the size range of the block copolymer domain.

Furthermore, by using *(S7)* and *(S9)* we can determine that

$$e_D = 0.003 * e_0 \qquad \text{(S11)}$$

Estimating the correlation length of block copolymer pattern

It is well known that the average size of particles can be analyzed by the mean of X-rays.[2] The equation developed by Scherrer has successfully been applied to GISAXS[3] and afterwards also used to estimate the correlation length ξ of block copolymers.[4] The estimation of the correlation length of patterns of directed cylindrical block copolymers along their alignment direction by GISAXS measurements has recently been demonstrated.[5]

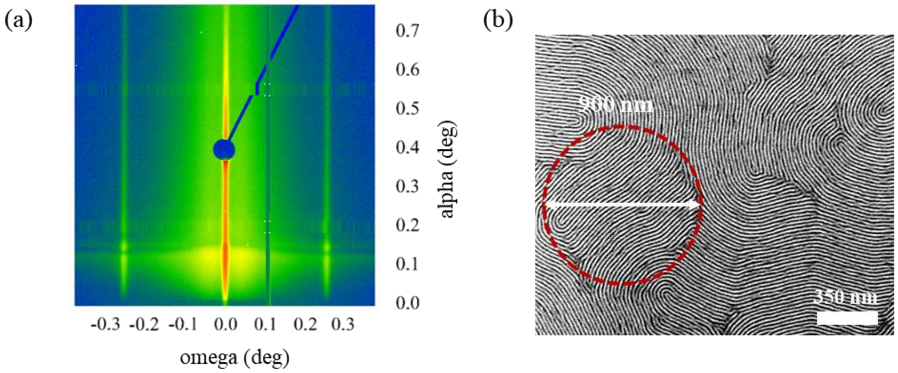

Figure S1: Analysis of a block copolymer fingerprint pattern by the mean of GISAXS and SEM. a): GISAXS pattern of a lamellar diblock copolymer self-assembled in finger print pattern, b): SEM image of the same sample as in a).

The correlation length ξ can be estimated as a function of the width Δq of the respective peak as follows:

$$\xi = \frac{2\pi K}{\Delta q} \qquad \text{(7),}$$

where K is the Scherrer constant, which depends on a variety of factors, like, among others, the shape of the grain and the unit cell.[6] In GISAXS the Scherrer constant for spherical grains accounts for 1.123, and 0.886 for platelets.[3] The peak data is fitted to Gaussian shaped peaks with the mathematical function

$$f(y_0, w, x_c, A) = y_0 + \sqrt{\frac{2}{\pi}} * \frac{A}{w} * e^{-2*\left(\left(x-x_c\right)/w\right)^2} \qquad (8)$$

with the fit parameters y_0, w, x_c and A. Here, x_c represents the peak center, y_0 is the baseline offset and A is the area under the peak. The parameter w is twice the standard deviation of a Gaussian distribution and relates to the peak *FWHM* as follows:

$$FWHM * 0.849 = w \qquad (9)$$

The *FWHM* is set equal to Δq to determine the correlation length. The determination of the correlation length based on the GISAXS pattern depicted in *figure S1 a)* yields $\xi = 903\ nm$. A comparison of *figure S1 a)* and *b)* confirms that the results yielded by the GISAXS and SEM analysis are comparable. Block copolymer correlation lengths in free surface in the range of few hundreds of nanometers have previously been determined by the analysis of SEM images.[7,8]

In the same manner, we have conducted an analysis of the width of the peaks depicted in *figure S2 a)-e)* to extract information about the correlation length ξ of the block copolymers inside the guiding patterns.

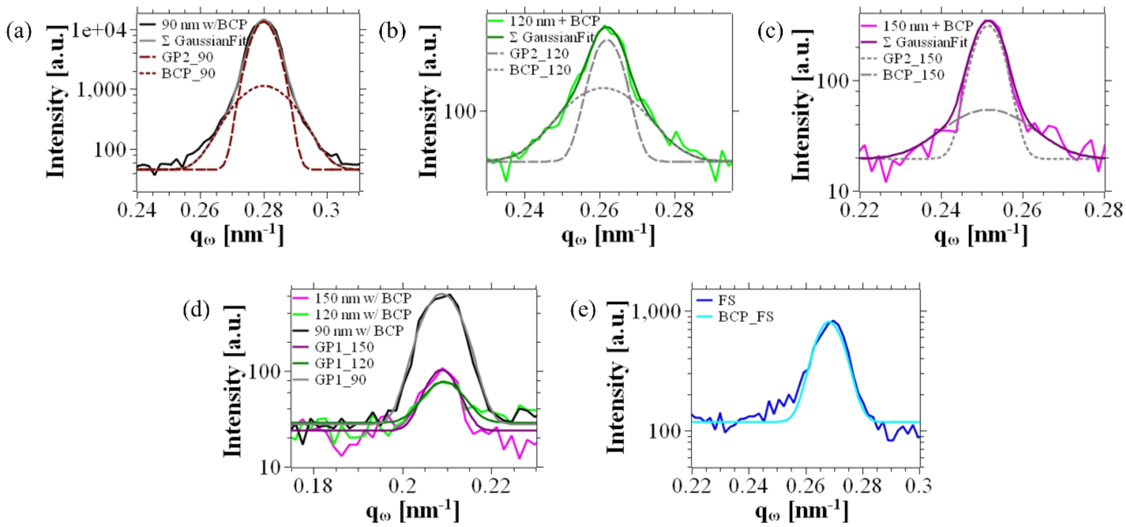

Figure S2: Analysis of all the peaks referred to during the analysis. a): double-peak fit of 4th GTR of 90 nm pattern with block copolymer, b): double-peak fit of 5th GTR of 120 nm pattern with block copolymer, c): double-peak fit of 6th GTR of 150 nm pattern with block copolymer, d):single-peak fit of 3rd GTR of 90 nm pattern, 4th GTR of 120 nm pattern, 5th GTR of 150 nm pattern (all patterns with block copolymer), e): single-peak fit of 1st GTR in free surface.

For the sake of clarity, we plot the fitted peaks separately in *figure S2 a)-e)*. Accordingly *figure S2 a)* depicts the measured 4th order peak of the 90 nm guiding pattern in black and the two fitted Gaussians in brown. In the same way, the result of the 5th order peak of the 120 nm guiding pattern is depicted in *figure S2 b)*, the 6th order peak of the 150 nm guiding pattern in *figure S2 c)*. To be able to compare the fits properly with GTRs that are not expected to contain signal originating from block copolymer scattering, the next lower order peaks are depicted in *figure S2 d)*. Furthermore, the cut through the free surface GTR we have analyzed before is plotted in *figure S2 e)*. In addition to that, we give an overview of the results in *table 1* providing the peak name, the associated periodicity and the relevant required to calculate the correlation length. The relevant values to determine the correlation length according to the *formulas* previously provided in this chapter are the peak width *w* according to *formula 7*, and the device and experiment dependent peak broadening B_{res} as proposed by Smiligies[3], which has been determined to be 3.26 µm^{-1}. This result is very close to the uncertainty reported for a similar experiment.[5] The estimation of the correlation length of the block copolymers is done using *formula 6* and yields 390 nm for the 90 nm pattern, 301 nm for the 120 nm pattern and 302 nm for the 150 nm pattern. The block copolymer pitch inside the 90 nm guiding pattern is compressed to 22.4 nm, while it is stretched to 24.1 nm and 25.0 nm in the 120 nm and 150 nm pitch guiding pattern, respectively.

GISAXS pattern	**Peak name**	**q_α [nm^{-1}]**	**d [nm]**	**FWHM [µm^{-1}]**	**w [µm^{-1}]**	**w - B_{res} [µm^{-1}]**	**ξ [nm]**
Free surface	BCP_FS	0.268	23.4	7.81	9.56	6.63	903.4
90 nm pitch	GP1_90	0.209	90.2	5.76	7.82	4.89	962.9
	GP2_90	0.280	89.8	4.38	6.65	3.72	1264.5
	BCP_90	0.280	22.4	14.22	15.00	12.07	390.1
120 nm pitch	GP1_120	0.209	120.3	2.29	4.87	1.94	2421.7
	GP2_120	0.261	120.5	5.32	7.45	4.52	1041.4
	BCP_120	0.261	24.1	18.39	18.54	15.61	301.7
150 nm pitch	GP1_150	0.209	150.5	4.22	6.51	3.58	1313.9
	GP2_150	0.252	149.9	4.40	6.66	3.73	1259.8
	BCP_150	0.252	25.0	18.34	18.50	15.57	302.4

Table S1: Overview of peak analysis results.

The discrepancy between the relatively low defect density observed in our SEM images and the low correlation length of the measured patterns may be related to the 3-D self-assembly morphology depicted in *figure 2 i)* in the main body. The small distortion of the structures in the guiding patterns may preclude the estimation of quantitatively accurate correlation lengths, because the distortion causes peak widening which is associated to a smaller correlation length. We may still compare the defect density in the different patterns, which represents one of the most important issues in block copolymer lithography.[9,10] Therefore we consider that the correlation length ξ is proportional to the defect density ρ_D^{-2} of the block copolymer pattern.[11] A mathematical expression to estimate the defect density ρ_D in a pattern with pitch p is $\rho_D \propto \frac{p}{\xi^2}$. This analysis shows us that in our experiments the defect density increases with the guiding pattern pitch, e.g. the multiplication factor (see *figure S3)*. We may, however, not forget that the block copolymer self-assembly depends heavily on the guiding pattern commensurability. Consequently, we present this measurement merely as a method to extract qualitative information about the defect density in the directed self-assembly of block copolymers from GISAXS patterns.

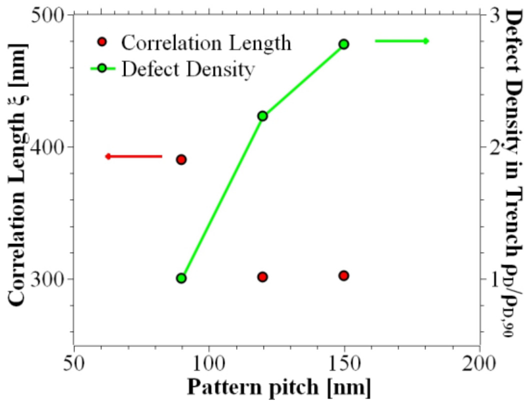

Figure S3: Estimating the correlation length of block copolymers in guiding patterns._Analyzing the correlation length based on FWHM analysis of block copolymer peaks (red dots) and the normalized defect density of block copolymers (green dots) as a function of the guiding pattern pitch.

Comments on figures 2 h) and 2 i)

It is well known that the cross-linked *HSQ* is preferentially wetted by *PMMA*.[12,13] It is also known that the exposure of *PS* to ionizing radiation promotes cross-linking[14], while in case of *PMMA* it leads to degradation.[15] This observation is confirmed by GISAXS experiments.[16] The required time for complete degradation / cross-linking of *PS* and *PMMA* thin films is determined to be in the range of various tens of seconds. Considering that both photon flux and photon energy in our experiment are significantly larger (i.e. 5.7 times larger photon flux and 1.6 times larger photon energy[16,17]), and the accumulated exposure time per guiding pattern in our experiment is in the range of few seconds, we expect the respective cross-linking / degradation process to have started. Based on the preferential wetting behavior and on the degradation of *PMMA* upon interaction with synchrotron radiation, we conclude that the recessed line in the middle of the area above the guiding patterns, as indicated by the black dashed lines, corresponds to *PMMA*.

This finding is different from what we usually observe in the tapping mode AFM analysis of block copolymers that have not interacted with synchrotron radiation.[18]

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