

Practice 2: Block Co-Polymers - Group 08

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1 Previous Work

1.a Questions regarding Ref. [1]

- a) Which parameters influence, whether a block copolymer self-assembles in a lamellar fashion, a cylindrical fashion or does not phase separate? Use the phase diagram of block copolymers to explain.

Two main parameters rule the self-assembly morphology in the studied di-block copolymers (BCP). On the one hand, there is the product between the Flory-Huggins interaction parameter χ_{AB} and the number of monomers per macromolecule N , which estimates the contact energy between the blocks per monomer in $K_B T$ units. On the other hand, there is the fraction of each macromolecule formed by one of the blocks, namely $f_j = N_j/N$ for the j -th phase, with N_j the number of monomers of block j among the N . For di-block copolymers $f_A + f_B = 1$, so talking about f_A alone suffices. If $\chi_{AB}N < 10.5$, following the phase diagram in Figure 1, a disordered phase emerges (no -microscopic-phase separation), whatever the fraction f_A be. Else, if the fraction f_A is around an even ratio 1/2, the BCP takes a lamellar morphology, for ratios around a third of the interval, the most likely morphology are ordered cylinders (of the minority block) surrounded by the majority block, while the minority block forms spheres periodically if the fraction f_A is closer to the boundaries. There are some additional more exotic phases like the gyroid or the closed-pack-sphere phase, that are also represented in the diagram. If f_A is too close to a pure homopolymer a disordered phase is formed. Note the implicit role of temperature. Because $\chi_{AB}N$ depends inversely with the temperature T and for a sample with a fixed ratio f_A the rest of parameters barely vary, decreasing T implies going upwards in the phase diagram, which broadens the ordered phase range in terms of the BCP composition.

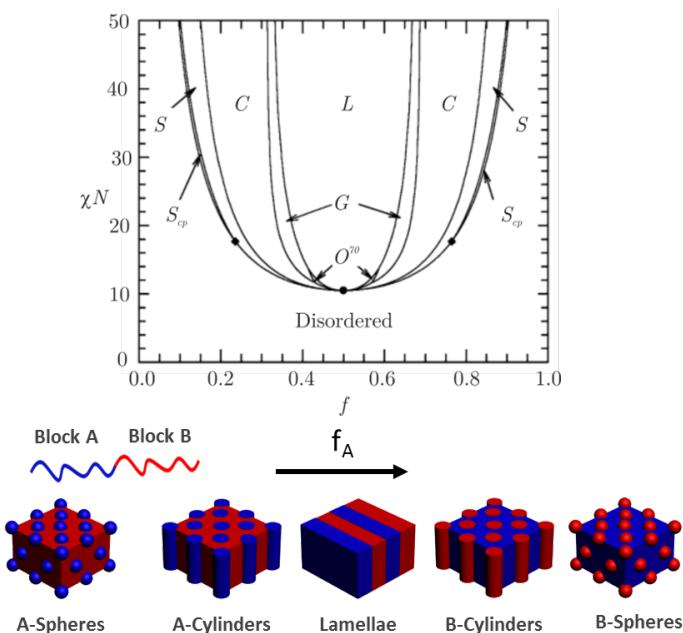


Figure 1: Theoretical phase diagram for di-block copolymers.

b) What is the Flory-Huggins interaction parameter and why is it important for the self-assembly of block copolymers?

The Flory-Huggins interaction parameter is given by:

$$\chi_{AB} = \frac{Z}{k_B T} \left[G_{AB} - \frac{1}{2}(G_{AA} + G_{BB}) \right] \quad (1)$$

It is the per-monomer difference between the interaction free-energy of the blocks G_{AB} and the average interaction energy between blocks of the same species with themselves G_{jj} , normalized to $k_B T$ units (times the number of nearest neighbours within a copolymer cell). If $\chi_{AB} > 0$, then $G_{AB} > 0.5(G_{AA} + G_{BB})$ and thus the interaction between the monomeres with their own species is more favourable, leading to a net repulsion between the blocks, which will be antagonized by the covalent link of the different blocks. If $\chi_{AB} < 0$, the crossed interaction will be more favourable, leading to a natural mixing of the blocks, be them covalently bonded or free.

This is a very relevant parameter for the self-assembly of BCPs (in particular, the positive χ_{AB} case) because it is the balancing of the force due to this driving free energy with the elasticity force due to the covalent bond between the blocks within the macromolecule, that gives a fixed ordered morphology to the BCP. In particular, the theoretical calculations used to draw Figure 1 heavily employ the balancing of the interaction forces with the entropic forces due to the linking between blocks.

c) How does the molecular weight of the block copolymer relate to its pitch?

The weight of the BCP is strictly proportional to N for a fixed pair of blocks AB . As explained in Ref. [1], a back of the envelope calculation leads us to a lamellar pitch of $\lambda \simeq 1.03 a \chi^{1/6} N^{2/3}$ with a the monomer size scale. This means that the bigger the molecular weight of the macromolecule, the bigger N will be and thus, the bigger will be the period of the lamella.

1.b Questions regarding Ref. [2]

a) What is a random copolymer? Draw a scheme of a block copolymer and a random copolymer to explain.

A “random” copolymer is a layer typically anchored to the substrate prior to the deposition of the block copolymer in order to control the surface energetics/affinity to each of the blocks A and B (if di-block) of the desired BCP. It is typically made of the same or similar monomers A and B as the BCP, which unlike in the BCP are polymerized in random sequences, impeding a proper self-assembly of this thin-film, which is in addition chemically anchored to the substrate via specific radicals. See Figure 2. The interest is that as a function of the fraction of one of the monomers of the BCP used, say A, one can control the affinity of the block A of the BCP to the surface plane.

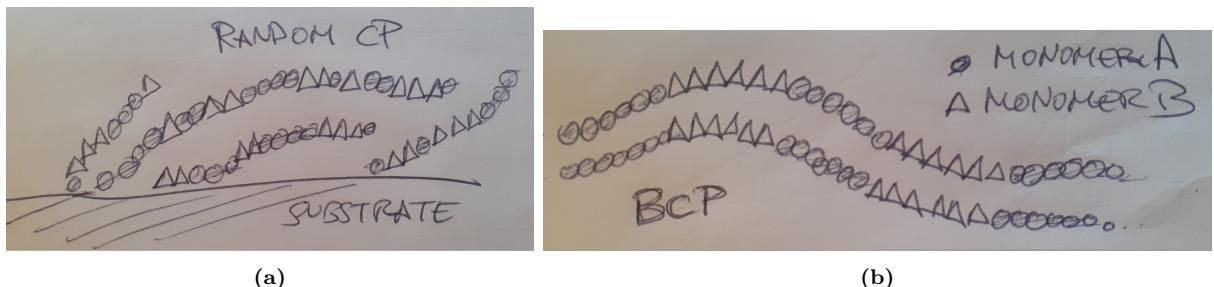


Figure 2: Sketch of a random copolymer in (a) and a Block copolymer in (b) as described in the text.

b) What are random copolymers used for in block copolymer lithography?

Random copolymers allow designing the direction in which the specific phase of the BCP will orient. For example, if the random copolymer has a high composition of monomer A, the substrate will have high affinity for the A blocks of the BCP. Then, if the morphology was lamellar, the planes of block A would orient along the surface, affine to A. The same would happen for B if the relative ratio of A in the brush was small. On the other hand, if it was a random copolymer with an intermediate A-B composition, then both planes of the lamella would try to wet the surface, yielding planes orthogonal to the surface. In the case of an alternative morphology like cylinders of phase B for instance, if the surface is affine to A then the cylinders would be knocked down over a plane of A. For an even composition of the random copolymer on the other hand, the cylinders would stand-up orthogonally.

All this allows chemical guiding of the morphology, which is useful for the posterior lithography process. There, one of the blocks is etched, and in the cavities (oriented as ruled by the random copolymer), photolithography and/or deposition is possible.

c) You have a symmetric block copolymer (50 % material A; 50 % material B) and spin coat a thin film of this material on a substrate coated with a random copolymer that consists of 80 % material A and 20 % material B. How do you expect the block copolymer to self-assemble? Draw your answer in a sketch.

Following the discussion on the phase diagram, the BCP will possibly take a lamellar/parallel plane morphology, which due to the higher affinity of the substrate to the material A, will lay down parallel to the substrate with a plane of A in contact with the random brush, as sketched in Figure 3.

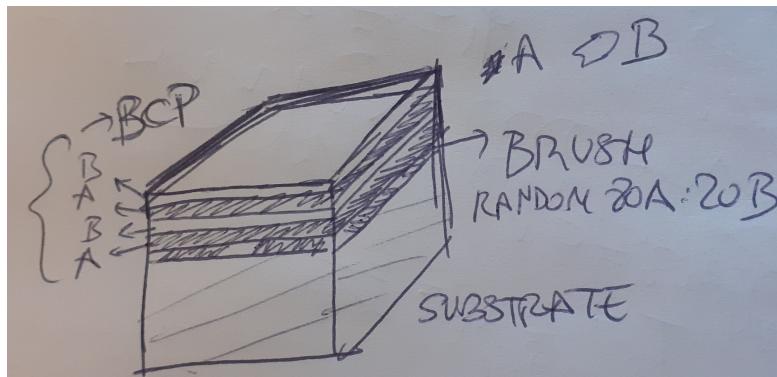


Figure 3: Sketch of a lamellar morphology oriented parallel to the substrate, following the text.

1.c Questions regarding the Experimental Protocol

a) We need to prepare 1.5% in weight solution of block copolymer in PGMEA (Propylene glycol monomethyl ether acetate) solvent. How much powder, in grams, we need to prepare 1mL of solution?

By approximating the density of the solution by the density of the solvent PGMEA 0.962g/mL due to the small amount of BCP, we get that 1.443 g BCP powder will be required for a solution of 1mL with 1.5% in weight BCP powder.

$$1\text{mL solution} \cdot \frac{0.962\text{g solution}}{1\text{mL solution}} \cdot \frac{1.5\text{g BCP powder}}{100\text{g solution}} = 1.443\text{g BCP powder}$$

b) In order to graft the brush layer into the substrate, we will follow the steps described in part B of next section (spin coating, thermal annealing and PGMEA rinse). Do you think is important the thickness of the spin-coated random layer?

If we were to use the brush as guiding pattern for the BCP in the walls of a lithographed channel for example, it would be important to fine-control the width of the random copolymer in all the steps. However, we are depositing the BCP in a plane surface, which makes its width less of a concern, even if a too wide final brush may add instability to the overall structure of the BCP over it. However, with our followed protocol, to a great extent, the width of the spin-coated random layer is irrelevant (from a certain thickness and on), since when rinsing the surface before the BCP deposition, the chains that do not get anchored to the surface will fade away.

2 Sample Characterization using SEM

In what follows, we proceed to characterize the morphology and orientation of four problem samples where block co-polymers (BCP) have been deposited on a functionalized surface. The objective is to guess qualitatively the relative ratio of the constituent blocks and the employed substrate functionalization, in addition to a quantitative determination of the dimensional features.

We know that the employed homo-polymers or blocks are Polystyrene (PS) and Polymethyl methacrylate (PMMA), and we know that the surface where the copolymers were deposited was either functionalized with a “random” BCP, featuring approximately a 1:1 ratio of each block and a random local orientation, or with a pure PS OH-terminal homopolymer. In addition, we known that each sample is due to a different block ratio and substrate functionalization, so we will be able to guess by elimination.

First Sample

We can see in Figure 4 a SEM image of the first problem sample. Lamellar curvy structures are appreciable, indicating an orthogonal orientation of different block planes relative to the plane of the substrate. Following the phase diagram discussion of the previous section, this suggests that the deposited block copolymer has an even ratio of PS to PMMA, since no spherical nor cylindrical structures appear to have been formed. In addition, the orthogonal orientation of the lamellas relative to the surface, suggests that the substrate was functionalised with an even “random” colopymer, featuring no chemical preference for either block of the BCP (both blocks attempt to wet the surface).

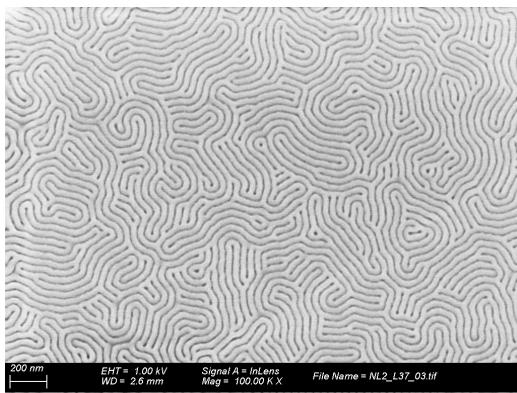
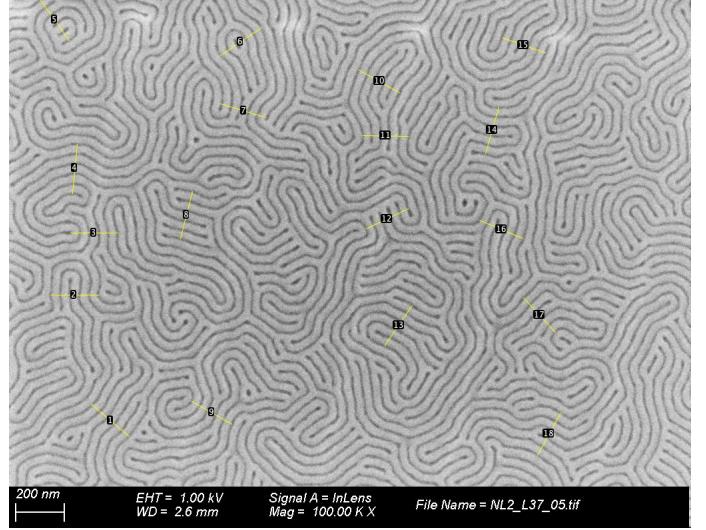


Figure 4: Example SEM image of the first problem sample. It appears to show standing lamellar surfaces.

We now proceed to estimate the period λ of the lamellar structures in the plane of the substrate, which consists of alternated PS-PMMA layers. In the SEM Figures, the white portions are known to be due to the PS, while the black regions are due to the PMMA. We measure such a period using two different approaches. On the one hand, we can estimate it by measuring the amount of pixels taken by a set of n consecutive lamellar black-white pairs, then divide it by n and convert it to nm using the amount of pixels taken by the scale of the SEM image. You can see the results of this in Figure 5, where we obtained an average period of 39.692 nm.

Line number	Length (nm)
1	203.252
2	200.704
3	199.296
4	201.603
5	205.211
6	204.891
7	199.465
8	199.155
9	190.979
10	196.604
11	192.274
12	195.957
13	200.323
14	196.563
15	193.077
16	193.554
17	193.251
18	198.458

(a)



(b)

Figure 5: In the subfigure (a) we can see the lengths of the measurements that appear in the subfigure (b).

On the other hand, one can compute the 2D Fourier transform of the SEM image and measure the magnitude of the main non-zero frequency component k . This is an angular frequency in pixel units that gives λ as $\lambda = 2\pi/k$, which can then be converted into nm using the scale of the image. See in Figure 6 the Fourier transform of the image of Figure 4. For this we wrote a Python script where the Fourier transform of each problem image is obtained and the average radius of the main rings are computed by frequency plane rotation. The details can be found in our Github repository [3]. This way, we obtain an average period of 39.22 nm in fair agreement with the manual computation.

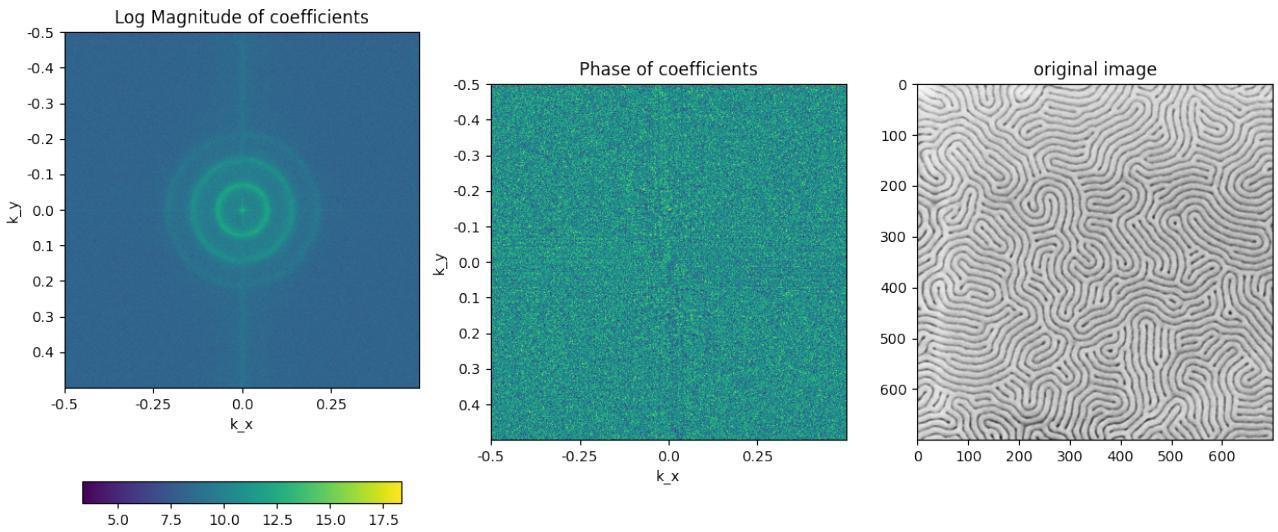


Figure 6: From right to left, the image cropped from the SEM image in Figure 4, the phase coefficients of its Fourier transform and the logarithm of its magnitude coefficients. All in pixel units.

Second Sample

We can see in Figure 7 an example of the SEM images taken to the second sample. In this case, we find a dotted pattern with a regular spacing forming an hexagonal 2D lattice. This suggests that the PMMA forms cylinders that are placed orthogonal to the substrate. In consequence, following the phase diagram discussion, the PMMA/PS ratio seems to be of around 1:3, while the substrate appears to have an even affinity for the PS matrix sustenting the PMMA cylinders and the cylinders themselves (the even “random” polymer functionalization).

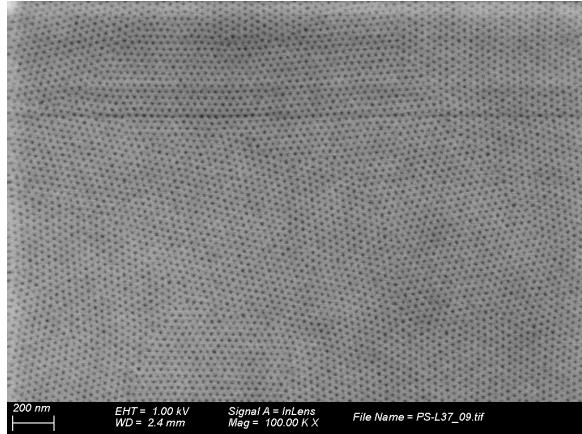


Figure 7: Example SEM image of the second problem sample. It appears to show standing cylinders.

Following the manual procedure, we find an average lattice periodicity (distance between two cylinder centers) of 35.403 nm. The measurements that we made in this procedure can be seen in Fig 8.

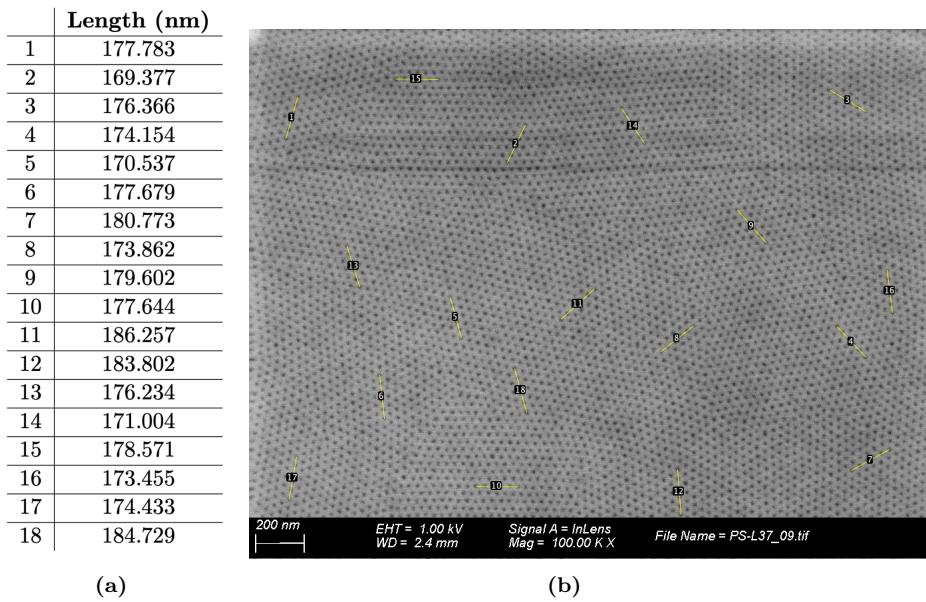


Figure 8: In the subfigure (a) we can see the lengths of the measurements that appear in the subfigure (b).

Using the Fourier transform, which can be found in Figure 9, we calculate an average parameter of 29.85 nm, given by the main frequency ring (of smallest frequency), which is due to the orthogonal distance from the center of an hexagonal cell to the boundary of a contiguous cell. It is the smallest distance between Bragg planes for the hexagonal lattice (even if strictly speaking is not a lattice parameter). Then, we can compute the distance between the centers of the cylinders using the Pythagorean theorem¹ to obtain 34.47 nm, in fair agreement with the manual measurement.

¹The inter-cylinder distance a is the cathetus of a half equilateral triangle, where the height h is the most frequent Bragg pattern. Thus $a = \frac{2}{\sqrt{3}}h$.

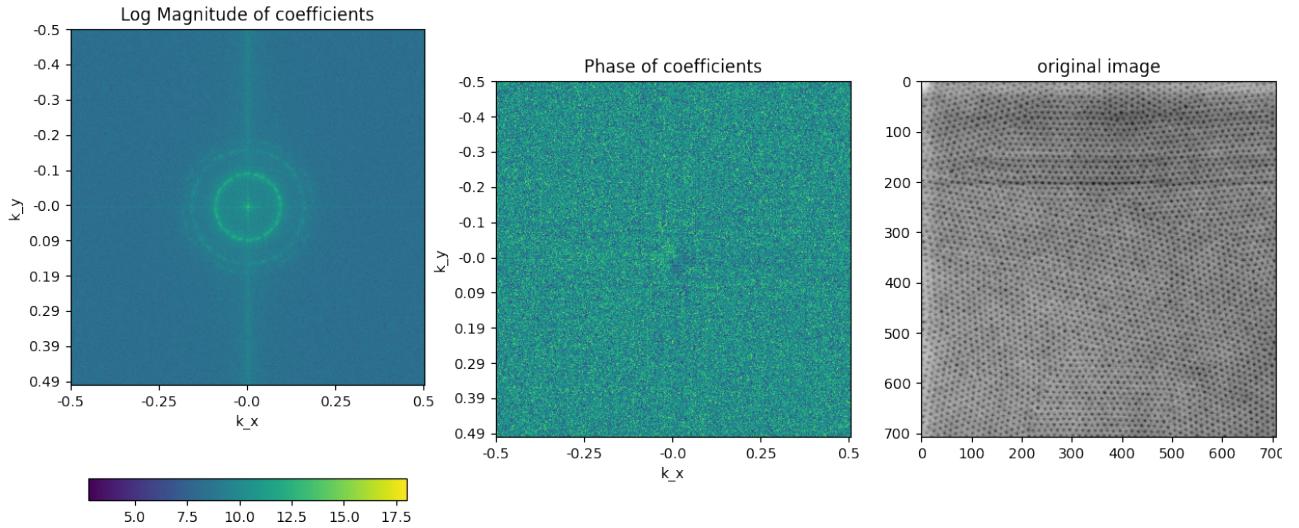


Figure 9: From right to left, the image cropped from the SEM image in Figure 7, the phase coefficients of its Fourier transform and the logarithm of its magnitude coefficients. All in pixel units.

Third Sample

We can see an example SEM image of the third sample in Figure 10. This shows an homogeneous plane of PS, which because it must be a BCP, indicates that parallel lamellar planes have been formed. Therefore, we know that the PMMA:PS ratio is quite even (around 1:1), like in the first sample, just that now the surface was functionalised with a PS-affine substance (like a random copolymer with main component monomers of PS kind). The holes just show that there is not enough material to cover the whole surface.

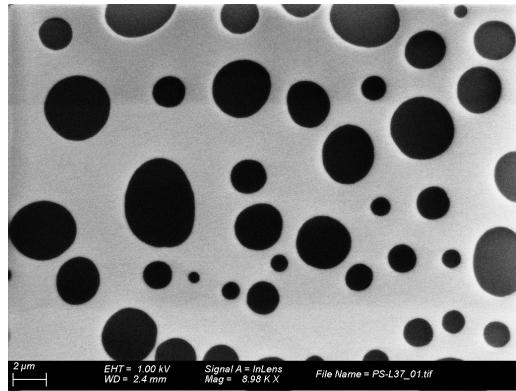


Figure 10: Example SEM image of the third problem sample. It appears to show a lamellar surface parallel to the substrate plane.

Fourth Sample

Finally, in the fourth sample in Figure 11, we find a structure similar to the first sample, just that now numerous “dot-like defects” are present. This could indicate that PMMA cylinders were formed, but that now most lay parallel to the substrate, except for some that happen to end up orthogonal to the surface. Because the option left is to have a PMMA:PS ratio of around 1:3 (forming cylinders) with a PS-affine substrate functionalization (thus cylinders would avoid touching the surface and lay horizontally), the hypothesis seems to be correct.

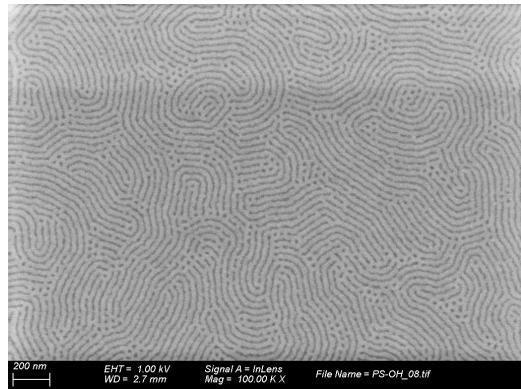


Figure 11: Example SEM image of the third problem sample. It appears to show cylinders that lay mostly parallel to the substrate plane.

Manual characterization, which measurements can be seen in Fig. 12 of the period between the knocked down cylinders gives us a period of 36,82 nm, while the radius of the main Fourier space ring in Figure 13 is found to be 35.92nm. Both of these numbers are close enough to the inter-cylinder distance of the second sample and far enough from the lamellar period in the first sample to use them as evidence in favour of the hypothesis that the curves are indeed knocked down cylinders (which are equally spaced as when they were orthogonal to the substrate).

Line number	Length (nm)
1	191,236
2	183,563
3	178,969
4	183,223
5	184,099
6	178,479
7	187,428
8	178,341
9	187,766
10	188,958
11	187,515
12	187,090
13	181,696
14	187,642
15	180,397
16	189,76
17	185,194
18	172,367

(a)

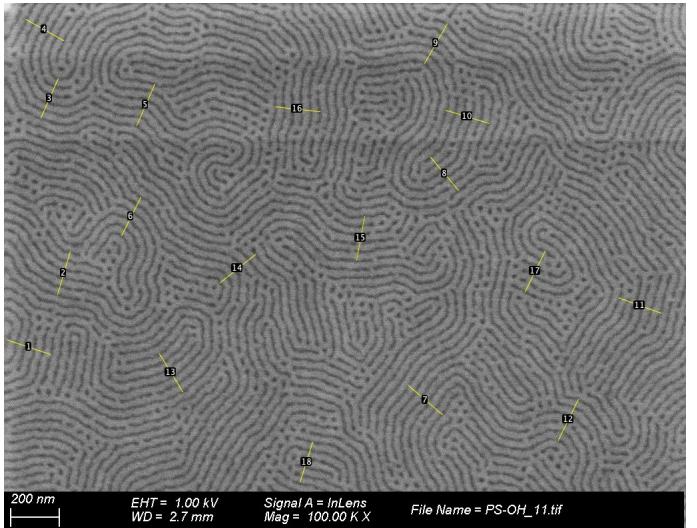


Figure 12: In the subfigure (a) we can see the lengths of the measurements that appear in the subfigure (b).

References

- [1] F. S. Bates and G. H. Fredrickson, “Block copolymers—designer soft materials,” *Physics Today*, vol. 52, no. 2, pp. 32–38, 1999.
- [2] P. Mansky, Y. Liu, E. Huang, T. P. Russell, and C. Hawker, “Controlling polymer-surface interactions with random copolymer brushes,” *Science*, vol. 275, no. 5305, pp. 1458–1460, 1997.
- [3] “Github repository with the code generated for the practice.” https://github.com/Oiangu9/_Miscellaneous/tree/main/NFab.

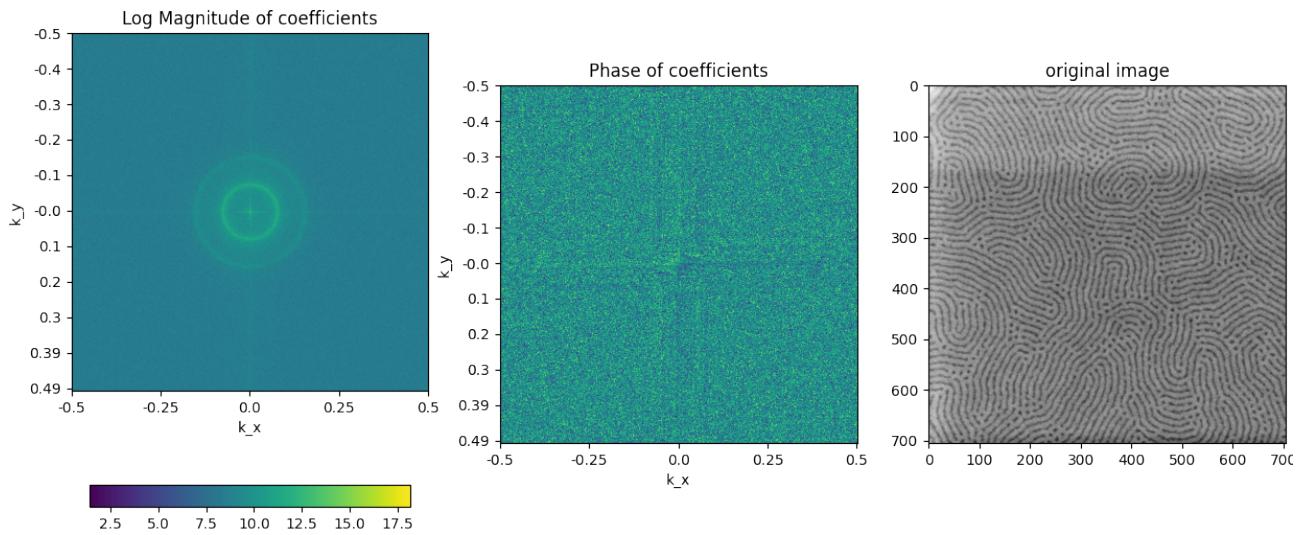


Figure 13: From right to left, the image cropped from the SEM image in Figure 11, the phase coefficients of its Fourier transform and the logarithm of its magnitude coefficients. All in pixel units.