



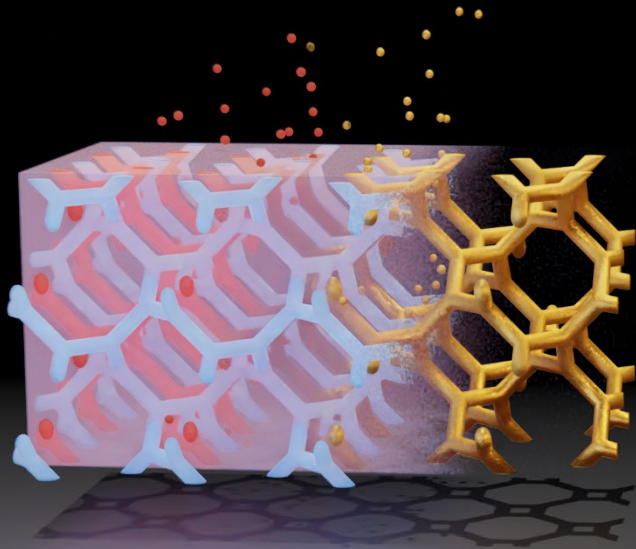
adolphe merkle institute
excellence in pure and applied nanoscience



**Swiss National
Science Foundation**

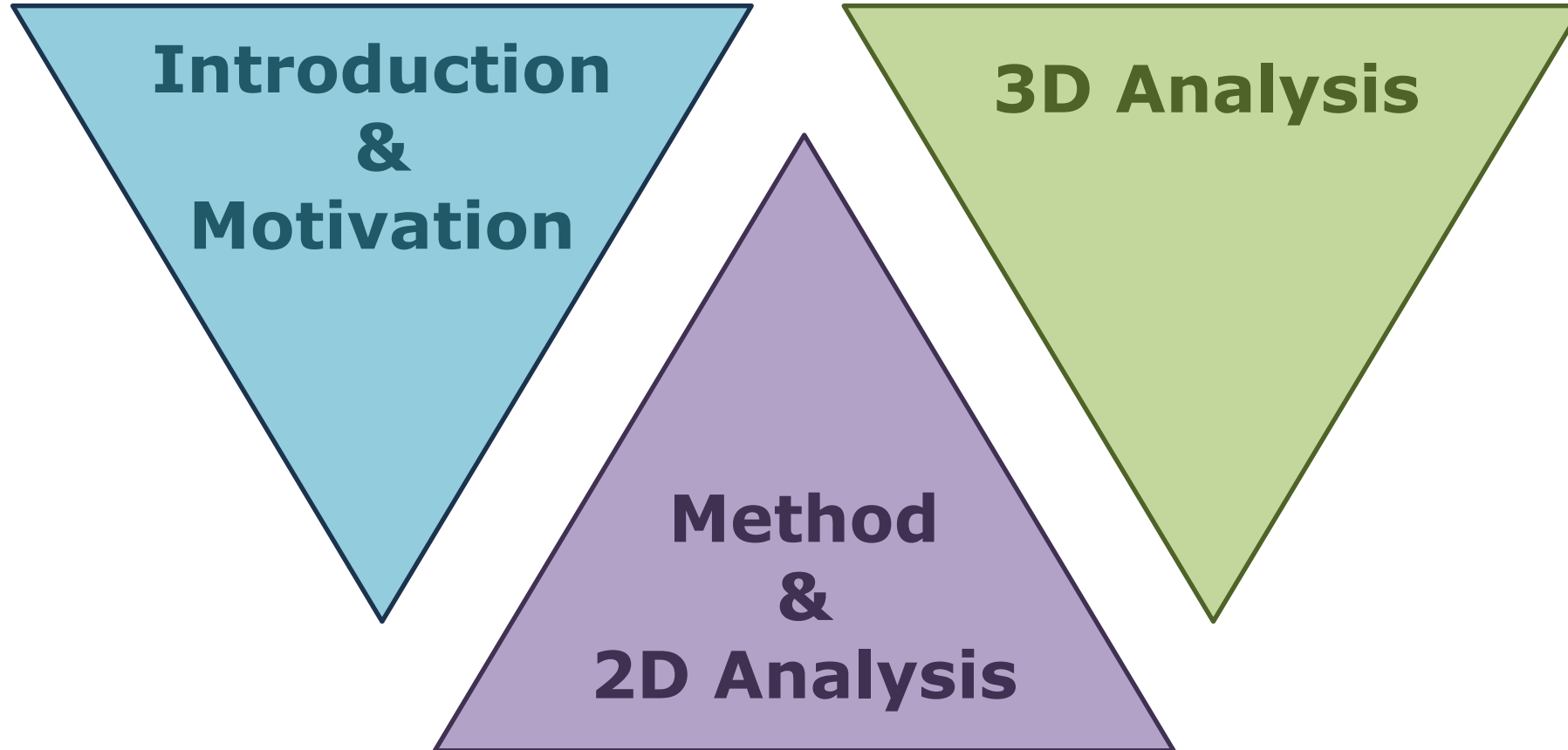


Large-Scale Ordered Block Copolymer Gyroid Films by Solvent Evaporation Annealing



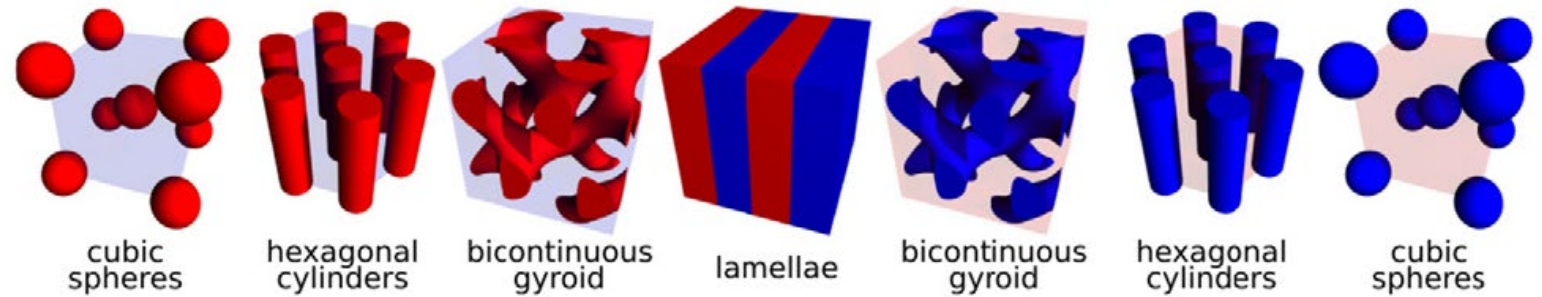
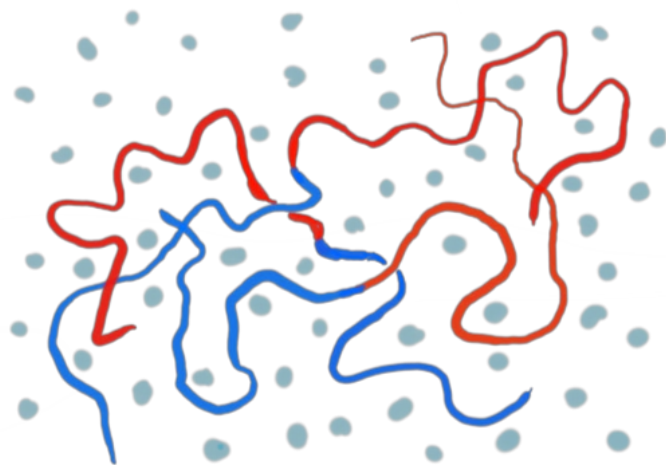
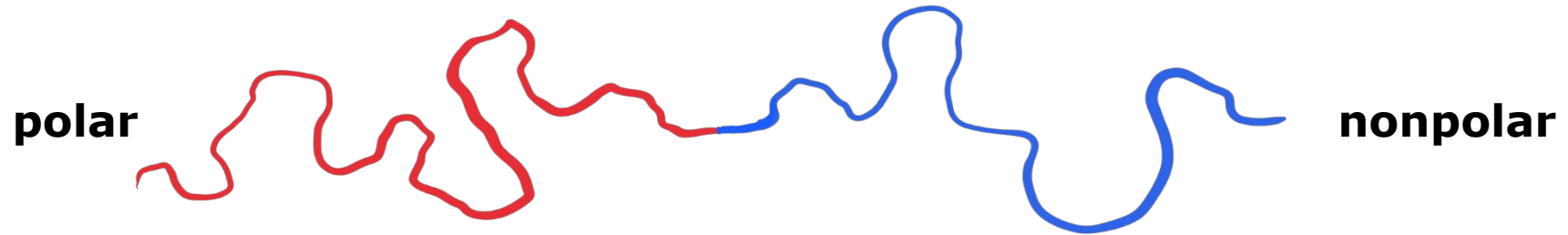
René Iseli, Doha Abdelrahman, Cédric Kilchoer, Narjes Abdollahi,
Brian van Büren, Jack Braden Bradford, Bodo Wilts,
Matthias Saba, Viola Vogler-Neuling, Ilja Gunkel, Ullrich Steiner

Adolphe Merkle Institute, University of Fribourg





Block Copolymer Self-Assembly

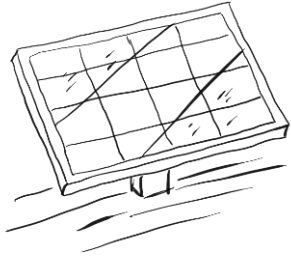


Polymer templates
Morphology dependent on length of Copolymers

Majewski Upton, Journal of Physics: Condensed Matter, Volume 28, 2016

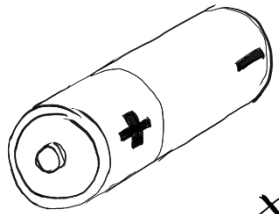


Applications



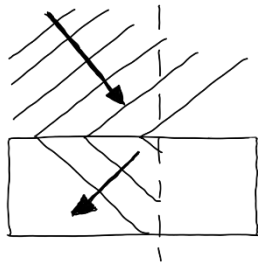
solar cells

optoelectronically active layer
templating for organic photovoltaics



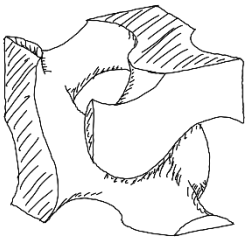
batteries

protective layer
charge transport



metamaterials

negative refractive index,
reservoir computing

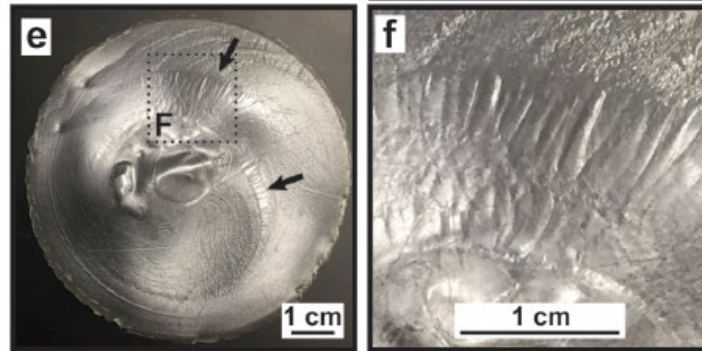
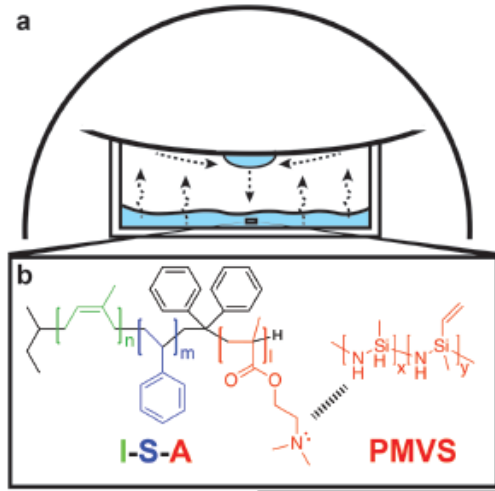


photonic crystal

structural color



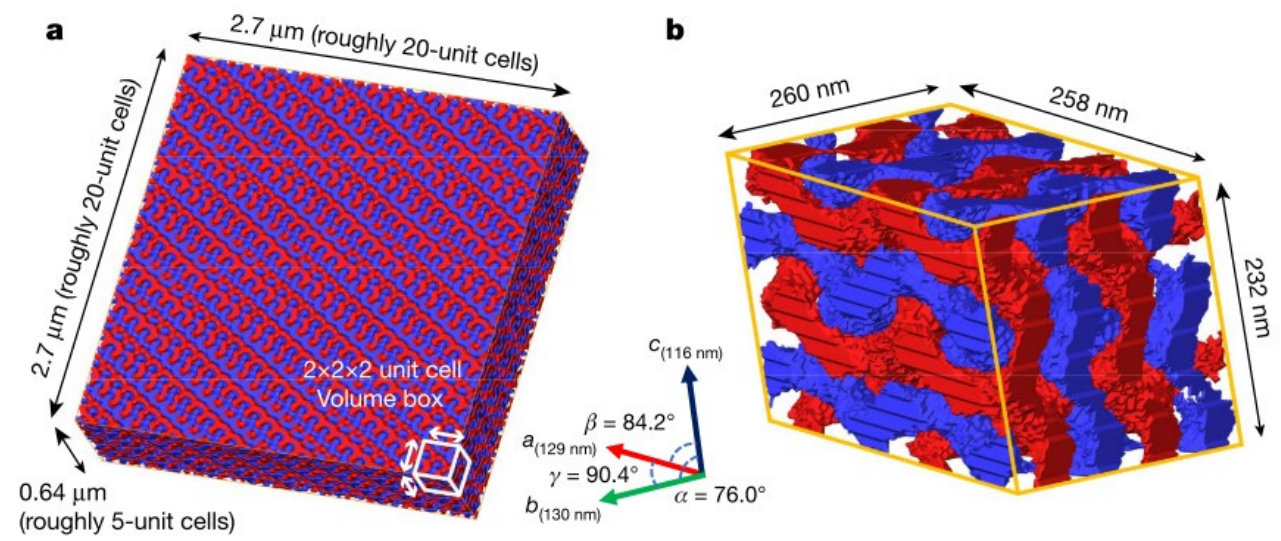
Goal: Control over the Self-Assembly



control over deformation

Susca, E. M., *Advanced Materials*, 31(40), 1902565, 2019

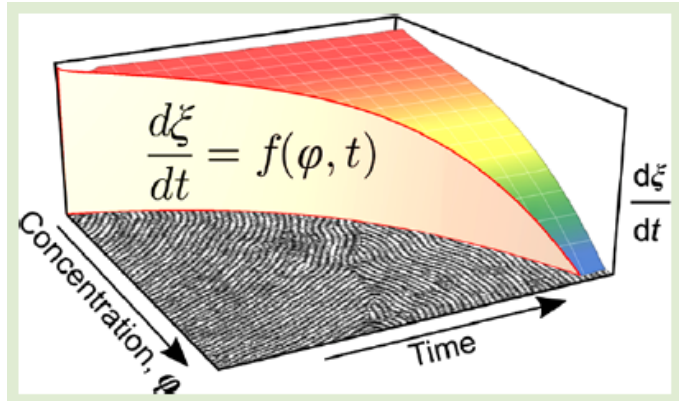
large homogeneous domains



Feng, X., *Nature*, 575(7781), 175-179, 2019

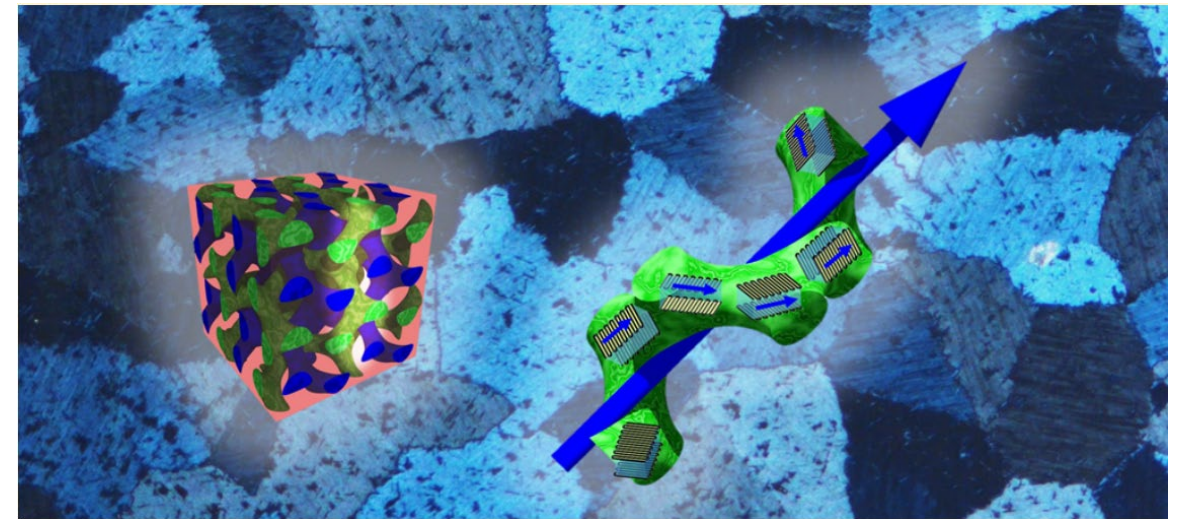
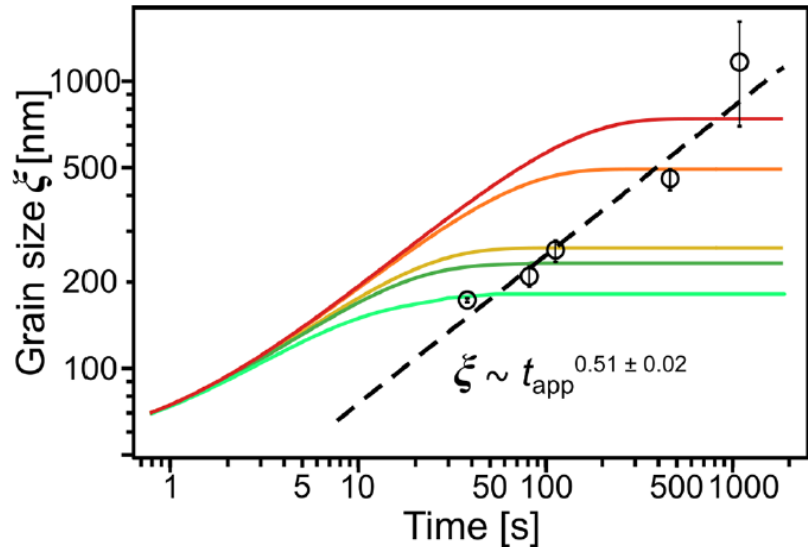


Approach: Combining two Successful Stories



Control over the domain size of 2D self-assembly
Solvent Evaporation Annealing (SEA)

To our group well-known, easy to analyse polymer system
poly**I**soprene-*b*-poly**S**tyrene-*b*-poly(ethylene **O**xide)
(ISO3)

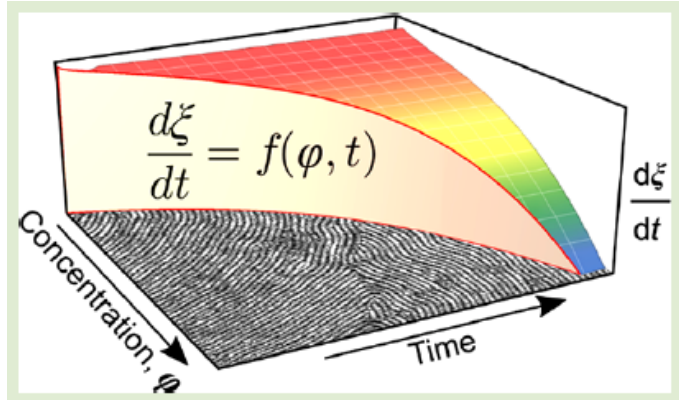


Leniart, A. A., *ACS Macro Letters*, 11(1), 121–126, 2022

Dehmel, R., *Macromolecules*, 50(16), 6255–6262, 2017

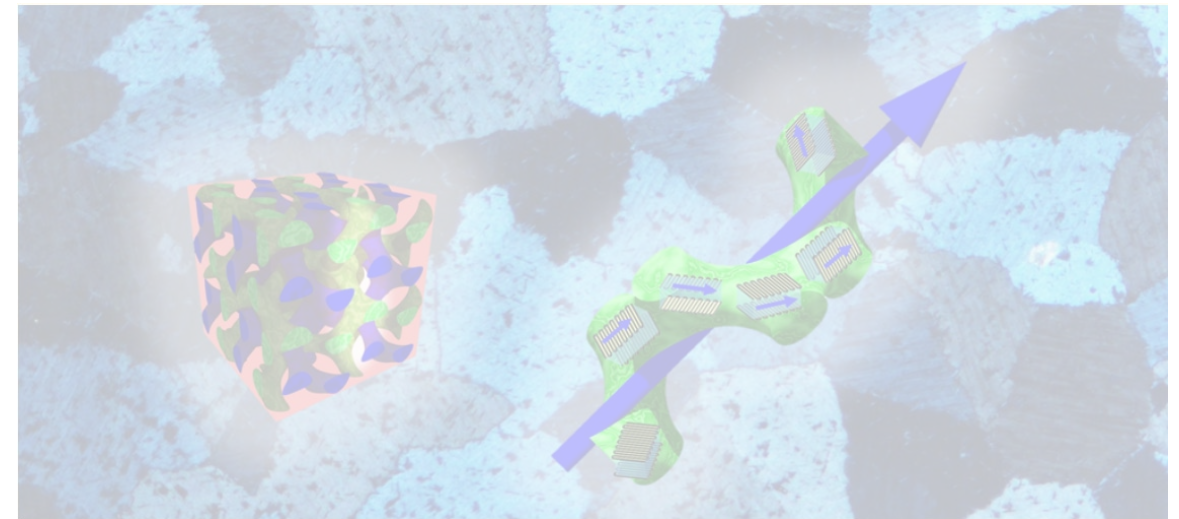
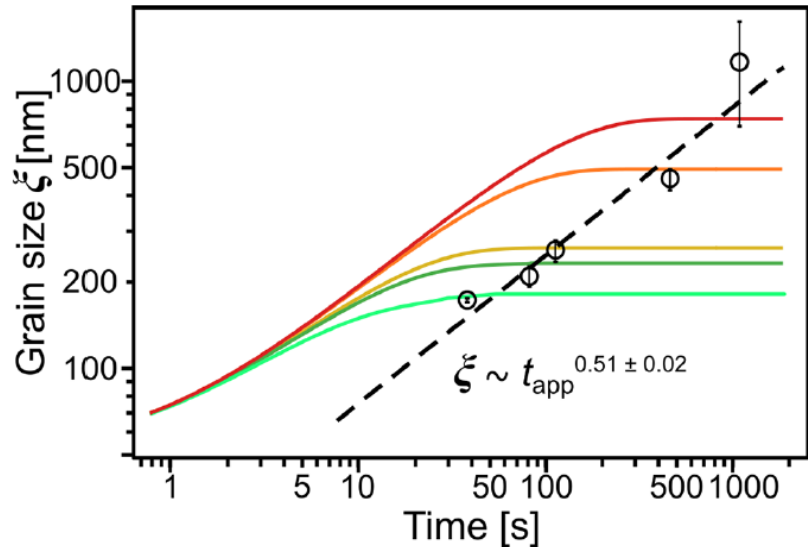


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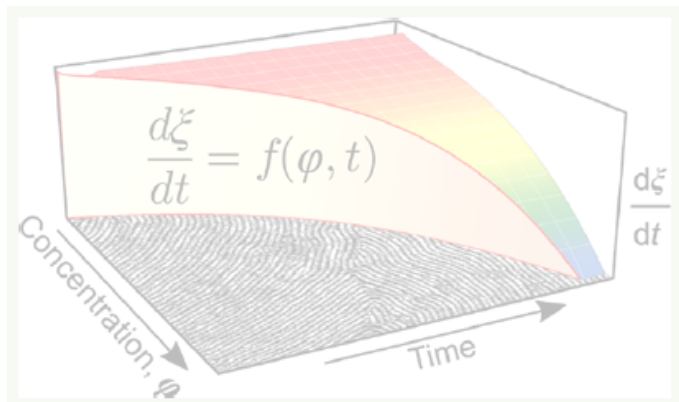
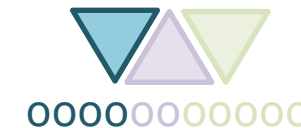


Leniart, A. A., *ACS Macro Letters*, 11(1), 121–126, 2022

Dehmel, R., *Macromolecules*, 50(16), 6255–6262, 2017

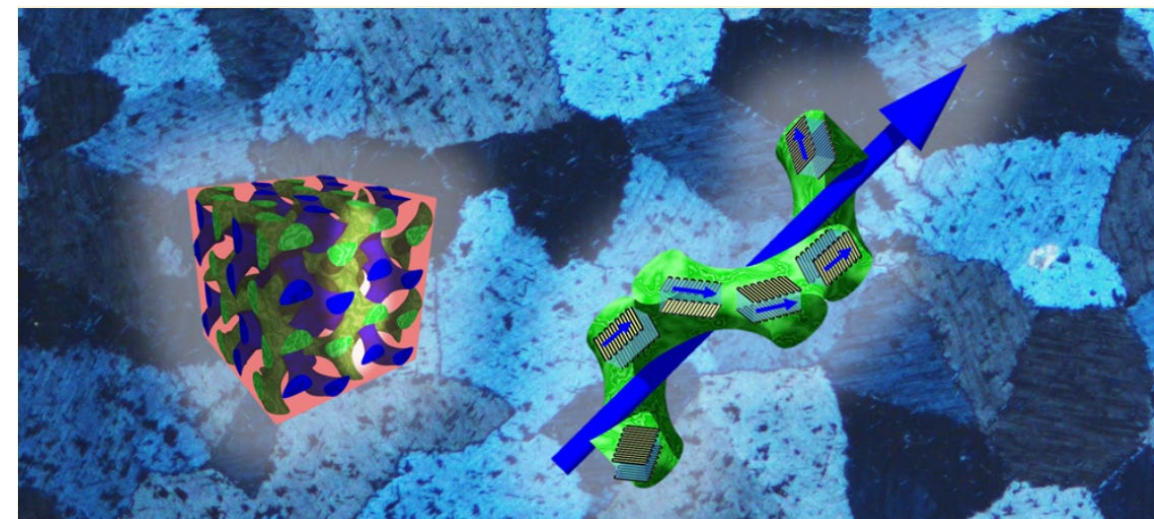
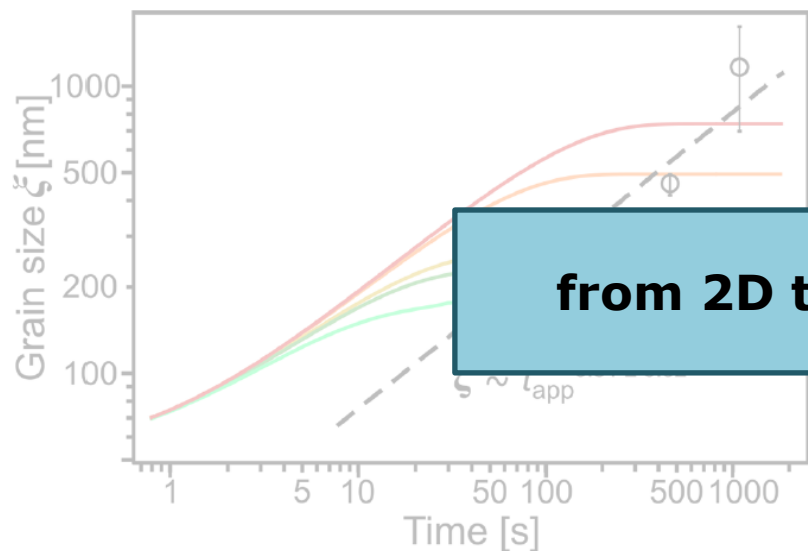


Approach: Combining two Successful Stories



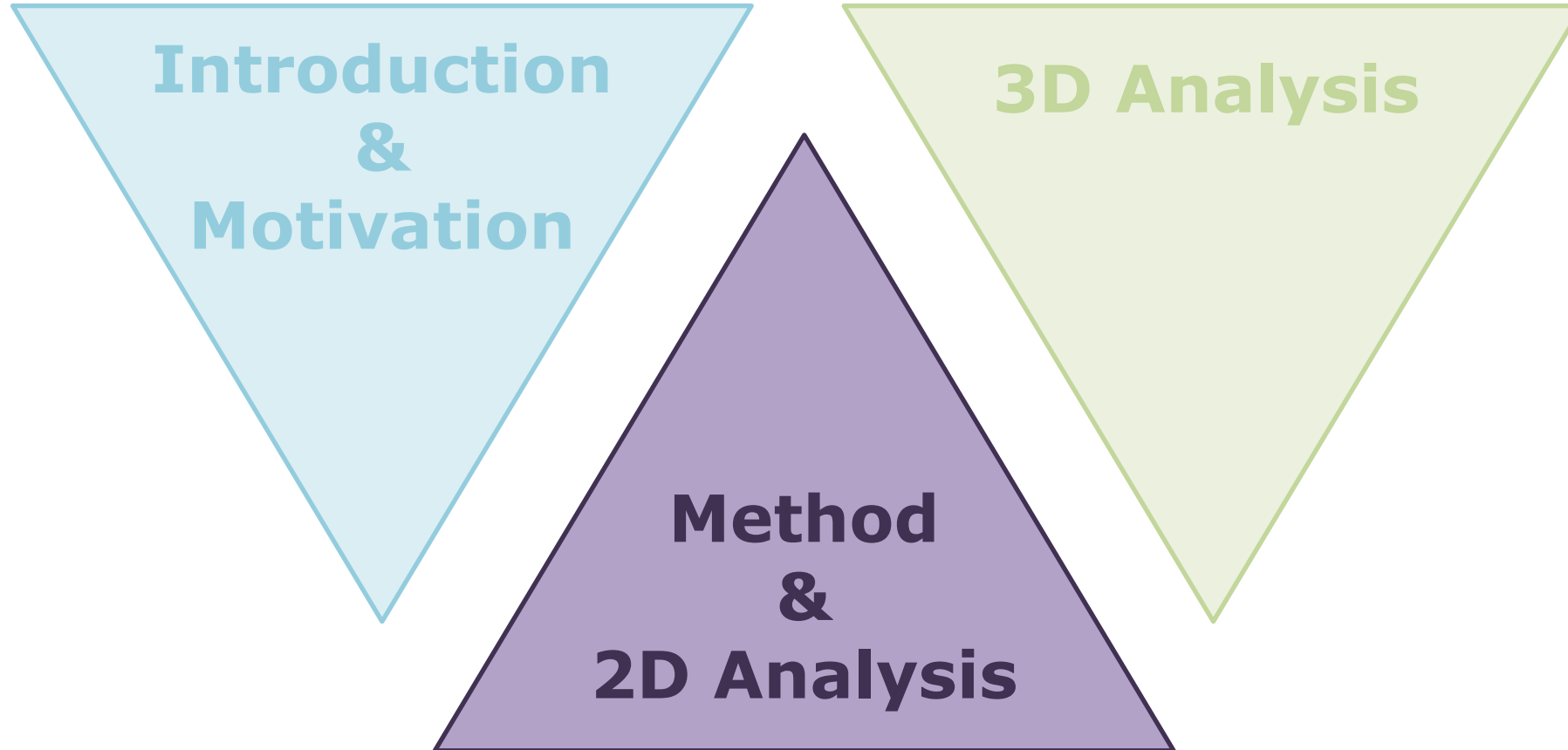
Control over the domain size of 2D self-assembly
Solvent **E**vaporation **A**nnealing (**SEA**)

To our group well-known, easy to analyse polymer system
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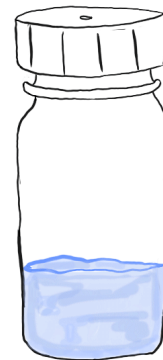
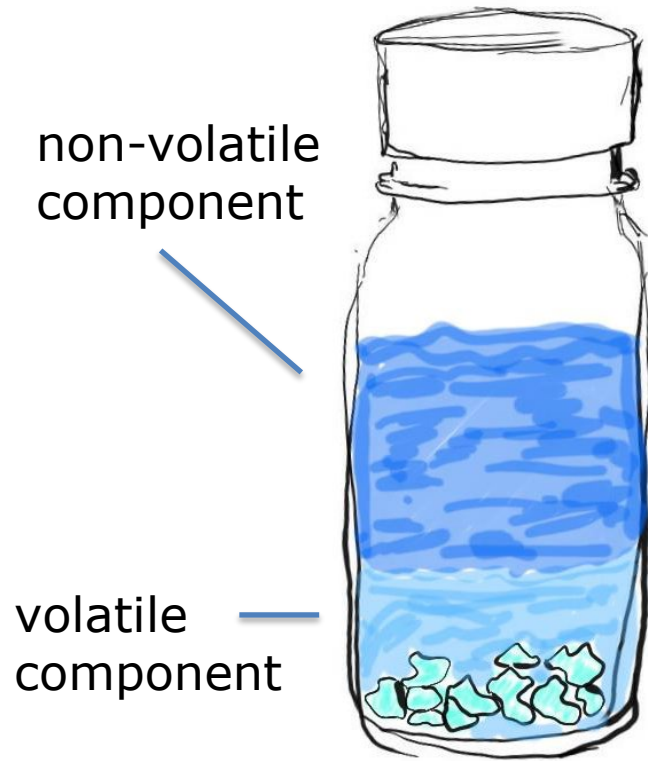
Leniart, A. A., *ACS Macro Letters*, 11(1), 121–126, 2022

Dehmel, R., *Macromolecules*, 50(16), 6255–6262, 2017

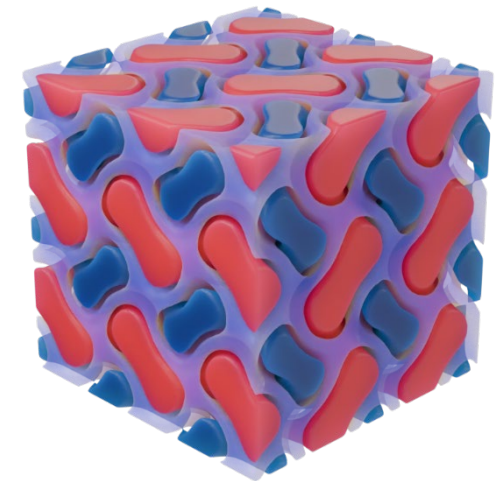
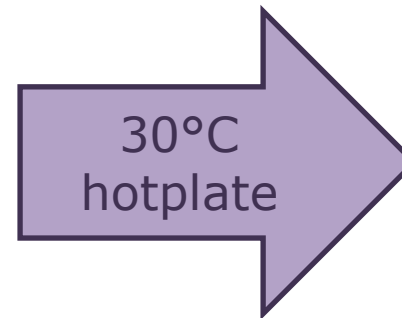




Method: Solution – Spin Coating – Drying

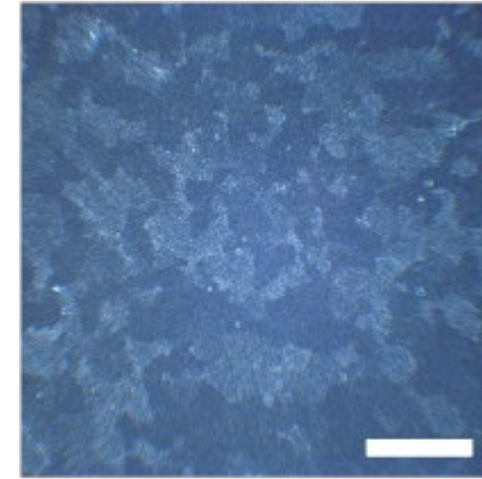
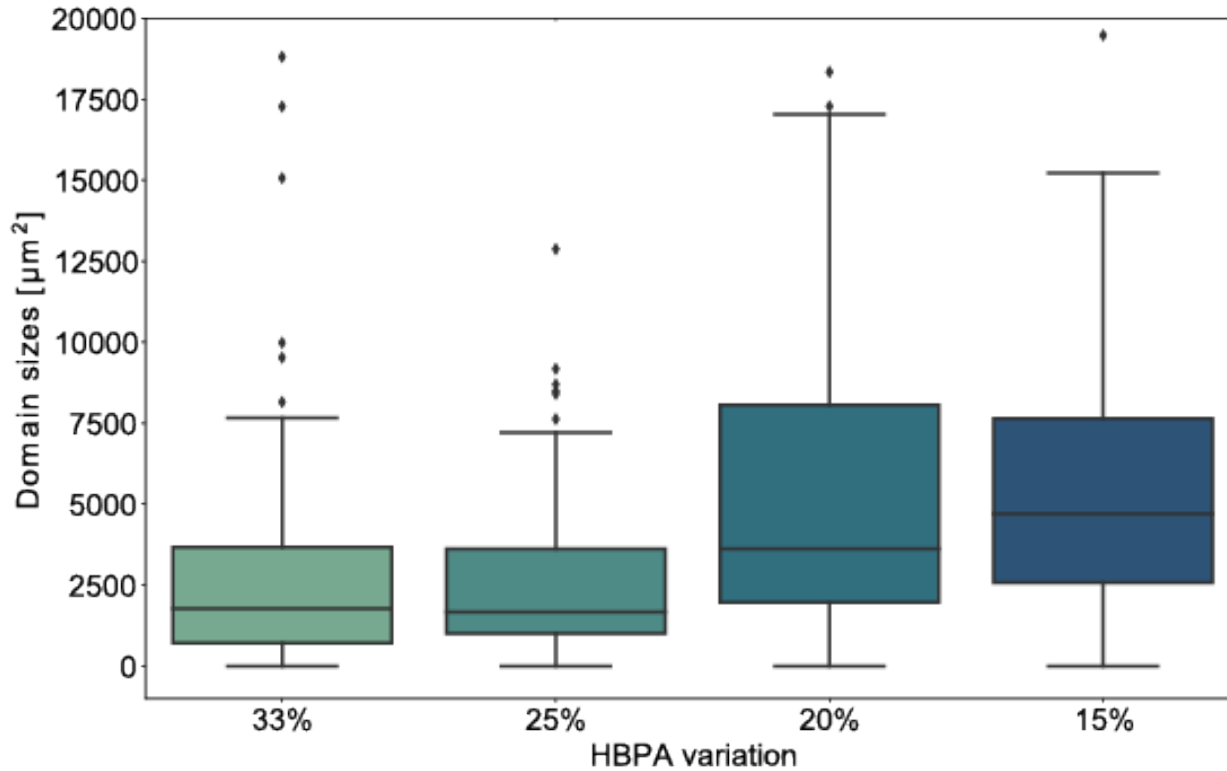


relatively **easy & fast** protocol

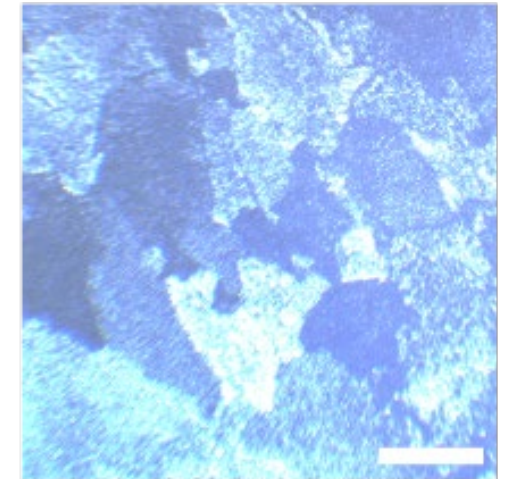




Grainsize Manipulation through SEA

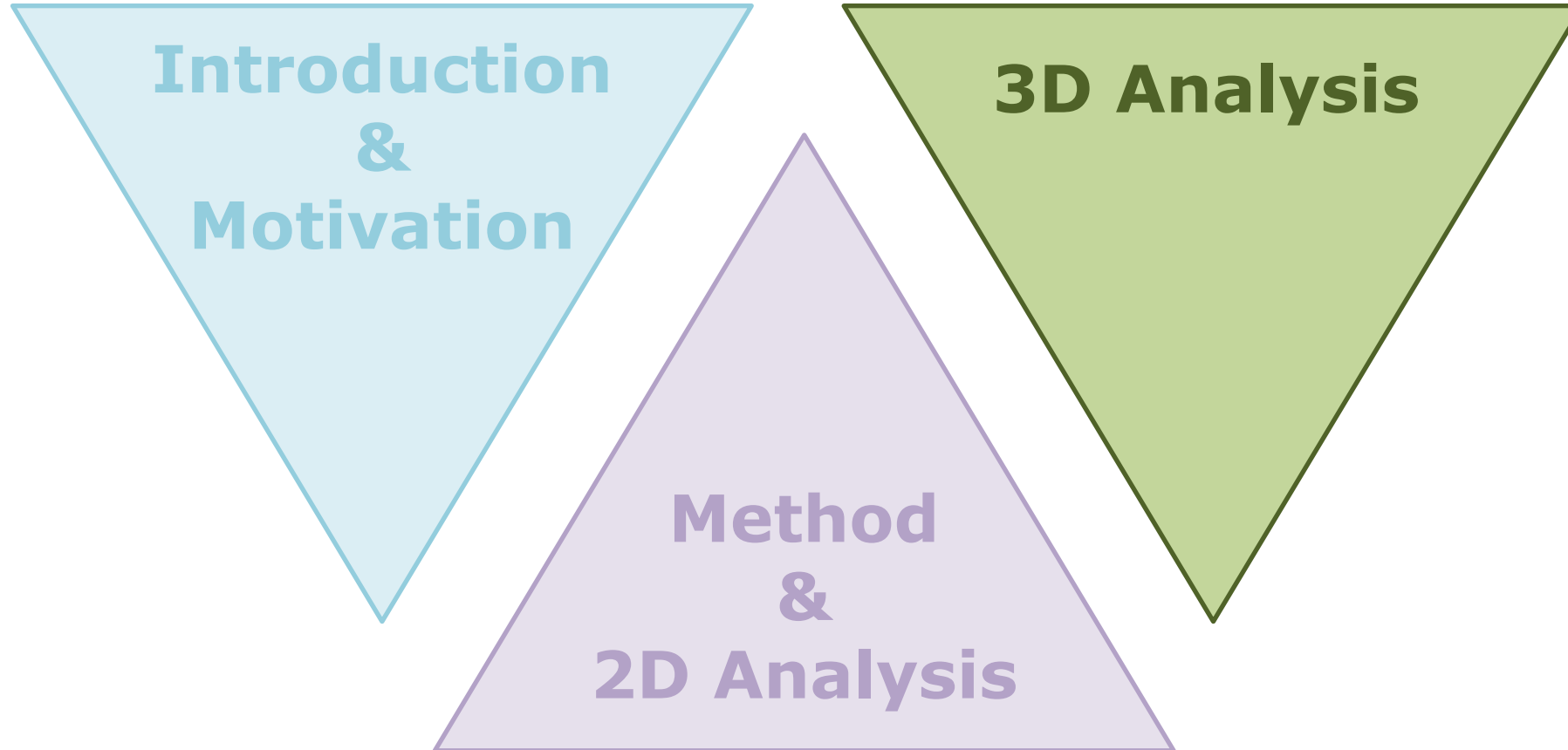


100 μm



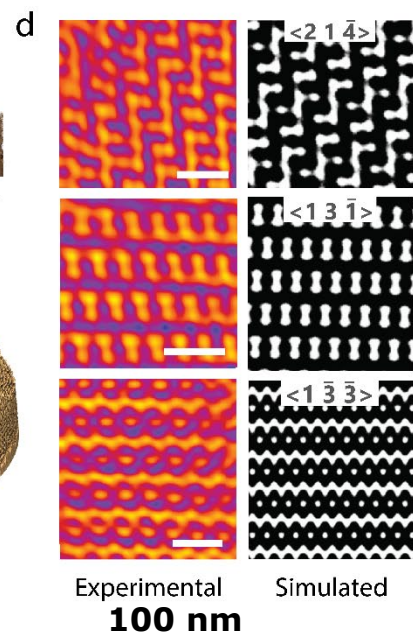
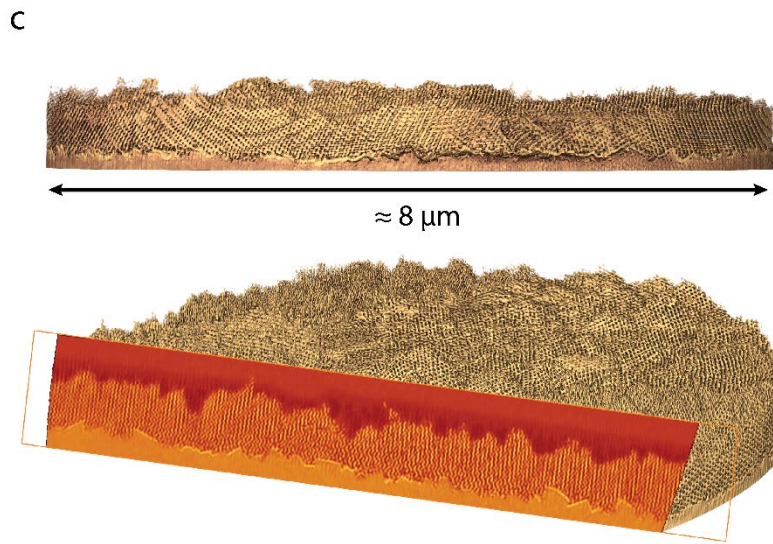
100 μm

cross polarized light microscopy shows **increase** of the **average grain size**



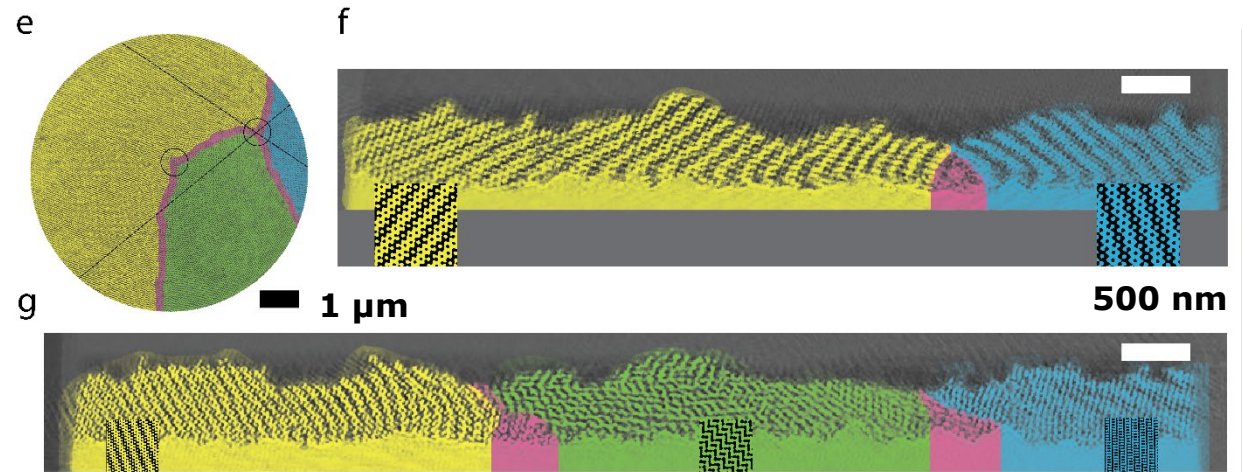


Analysing Polymer Templates



X-Ray Nanotomography

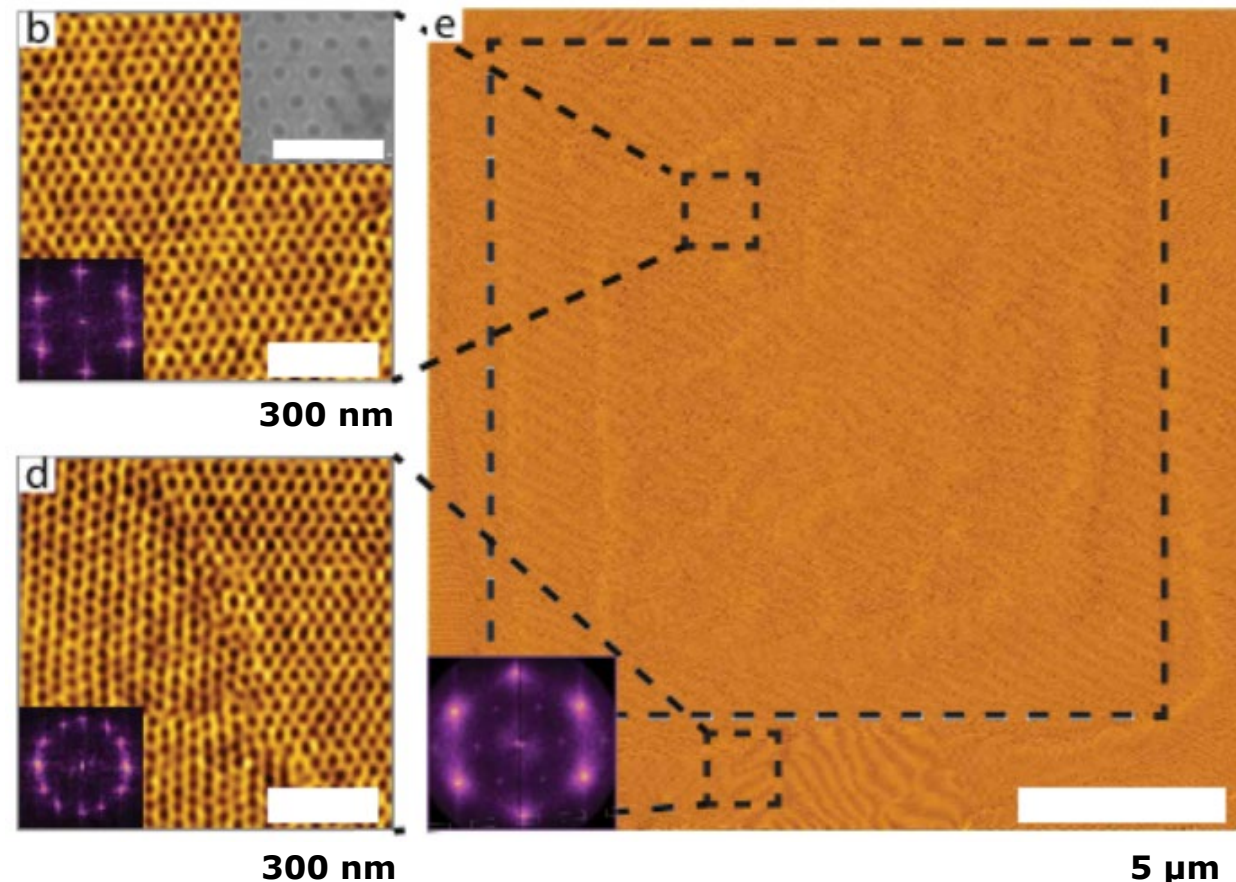
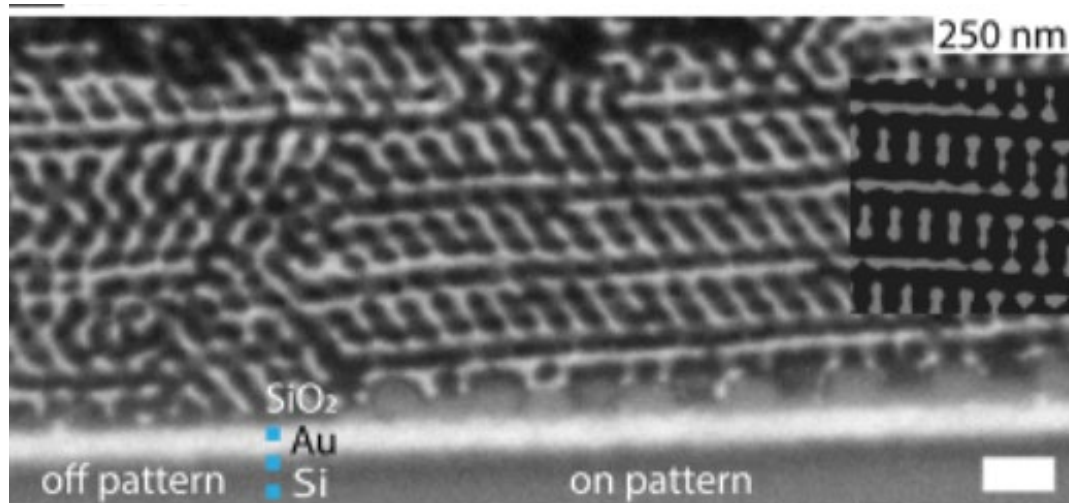
Large volumes & accurate
long processing time



Djedghdi, K., arXiv:2304.12027v2

Atomic Force Microscopy (AFM)

matching of surface and cross-sections
2 methods, manual matching

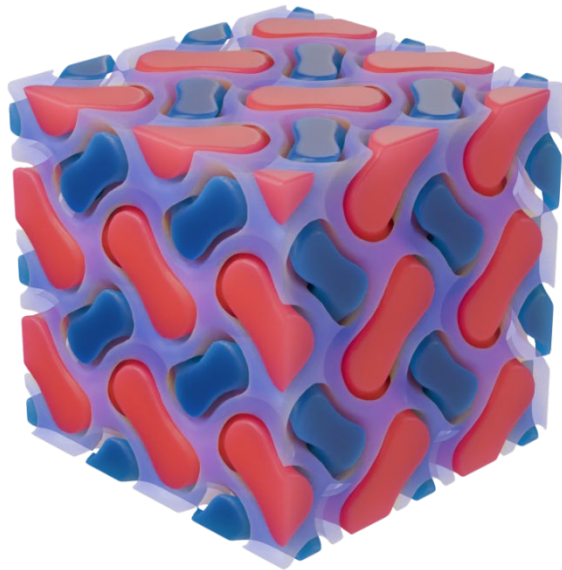


Focused Ion Beam (FIB)

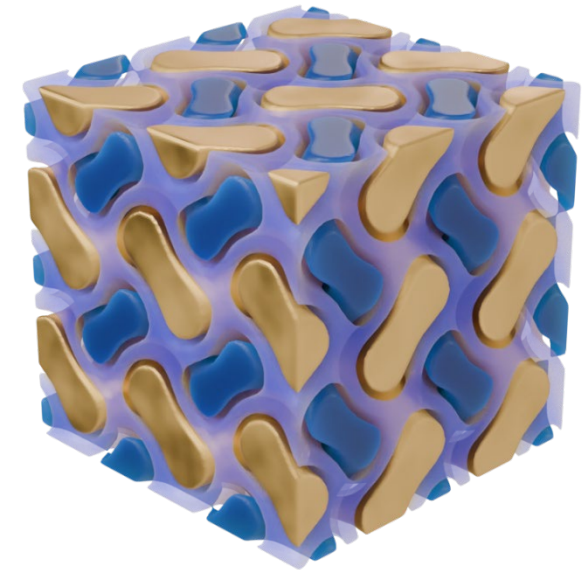
Abdelrahman, D., *ACS Applied Materials & Interfaces*, 15(50), 57981–57991, 2023



Preparing Samples for FIB Analysis

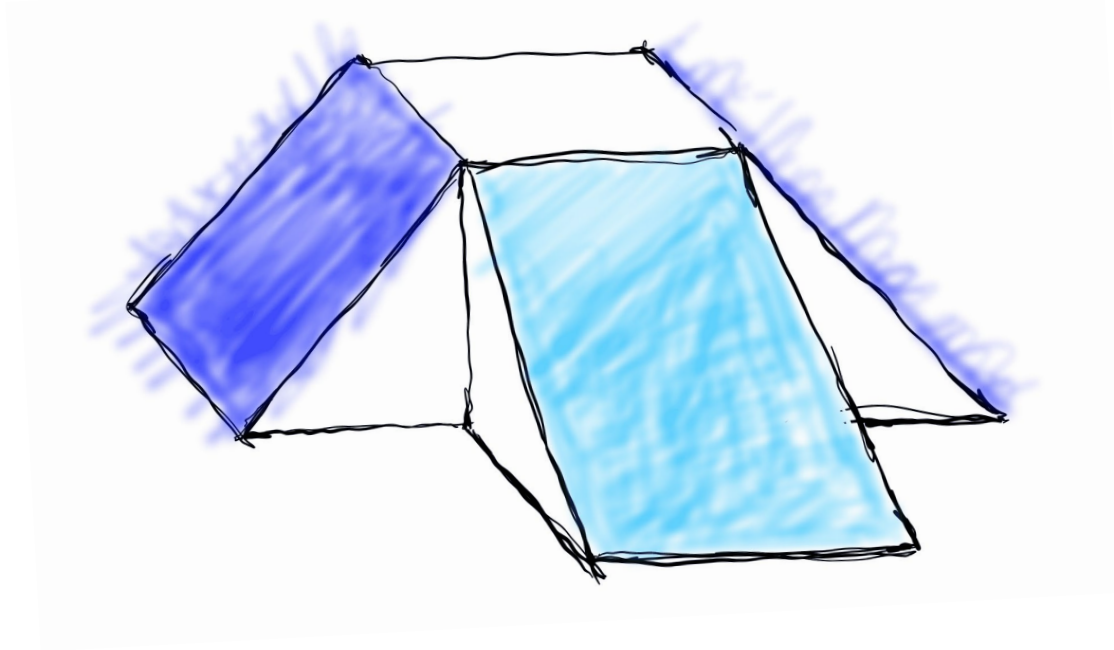


etching of PI system
electroplating of the voids





Focused Ion Beam (FIB) Cross Sections

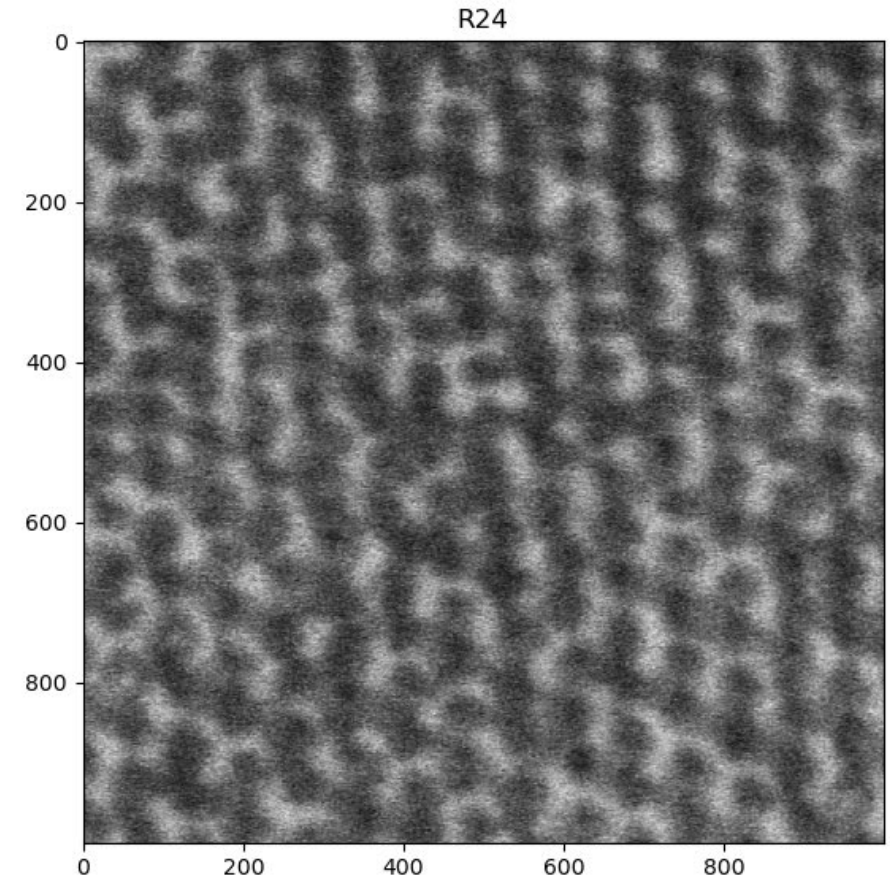
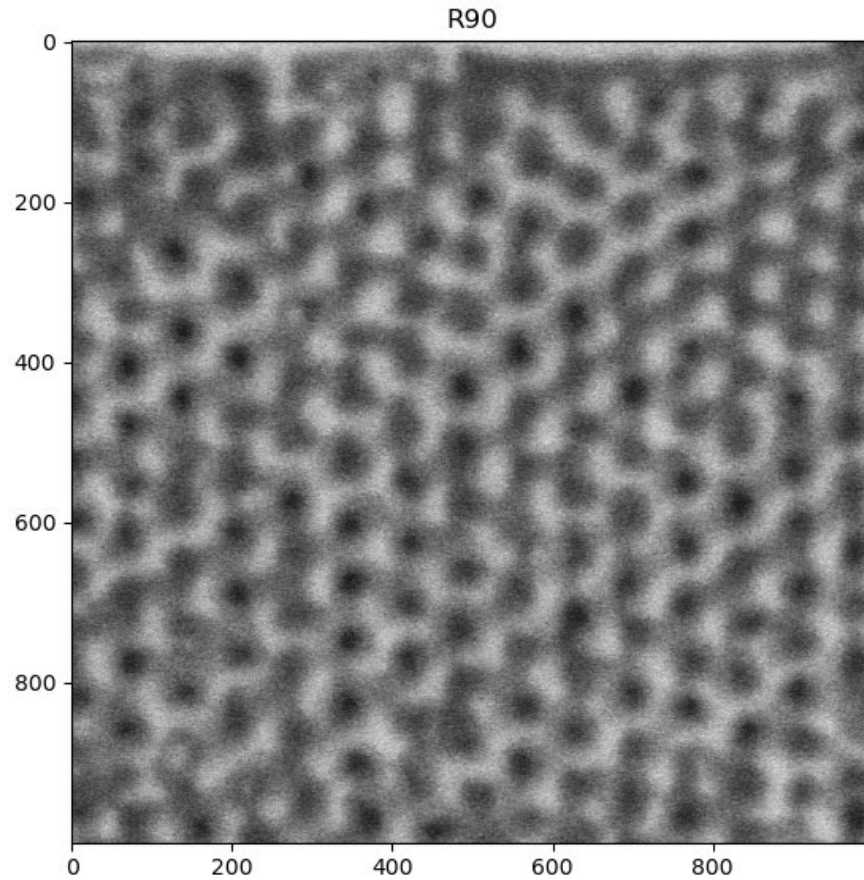


4-8 cross sections
of the same domain
while cutting at
different angles





Focused Ion Beam (FIB) Crosssections



**Automated
matching
of the cross
sections**



Adolphe Merkle Institute Soft Matter Physics:

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Dr. Ilja Gunkel
Dr. Matthias Saba
Dr. Viola Vogler-Neuling
Prof. Bodo Wilts

Fellow Students

Dr. Doha Abdelrahman
Cédric Schumacher
Dr. Cédric Kilchoer
Dr. Narjes Abdollahi
Bilel Abdennadher

Master Student

Brian van Büren

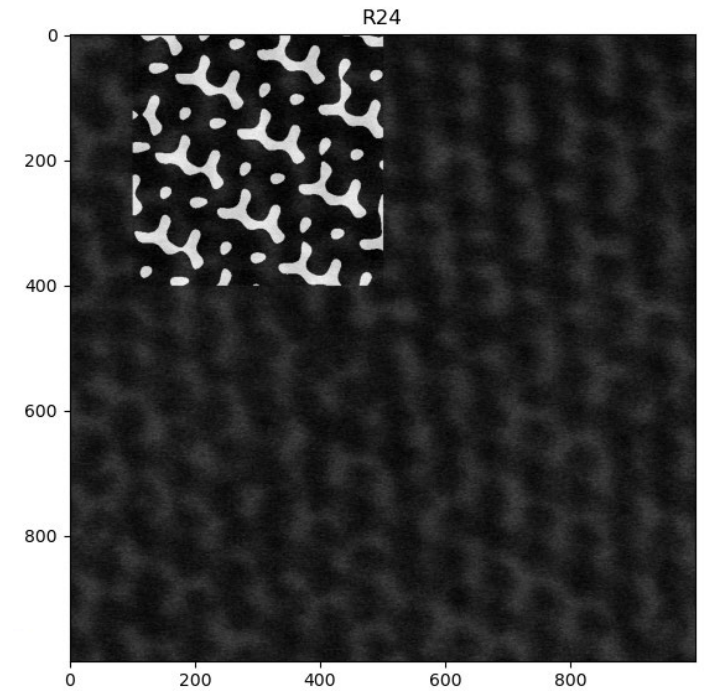
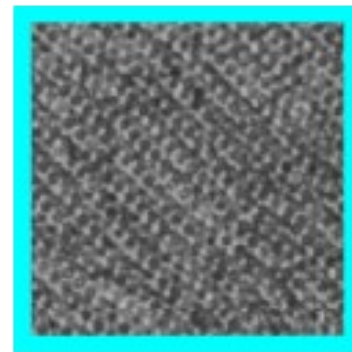
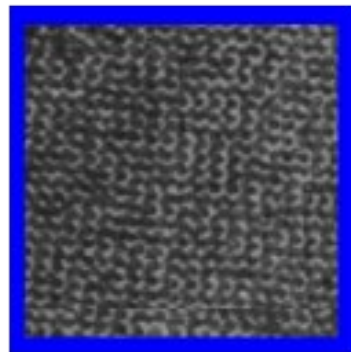
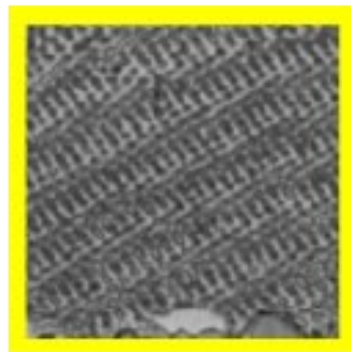
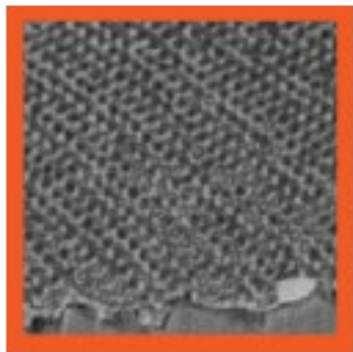
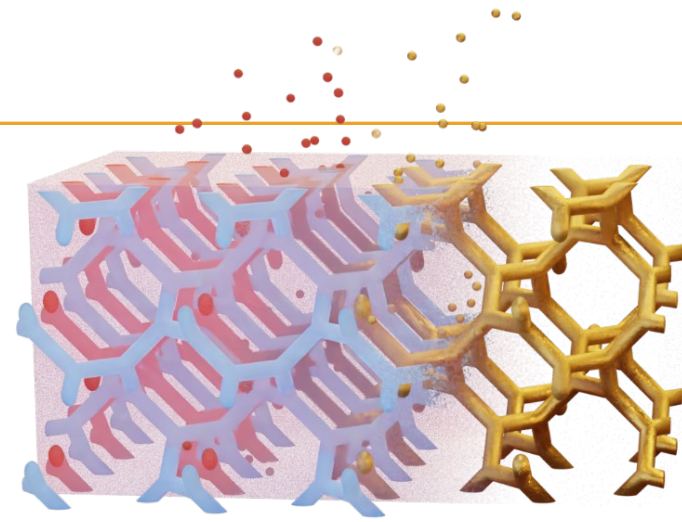
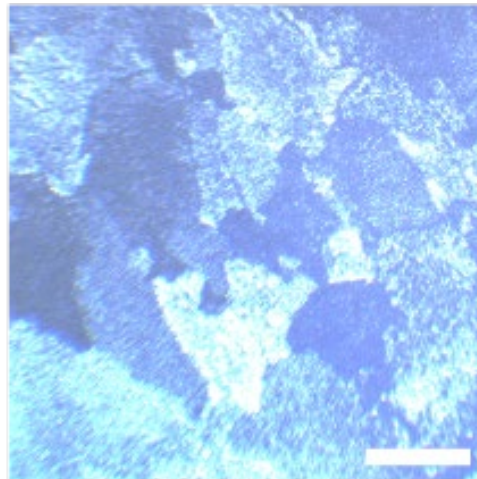
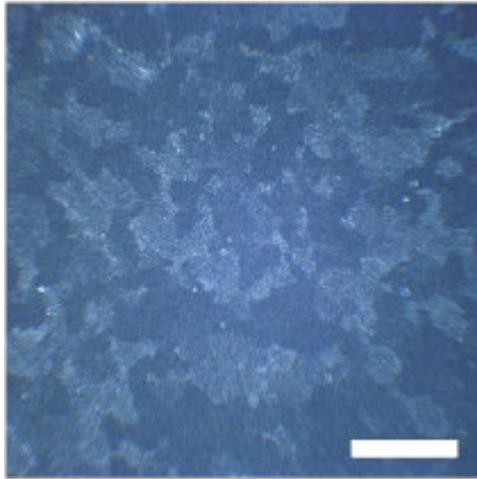
Summer Intern

Jack Braden Bradford





Questions?



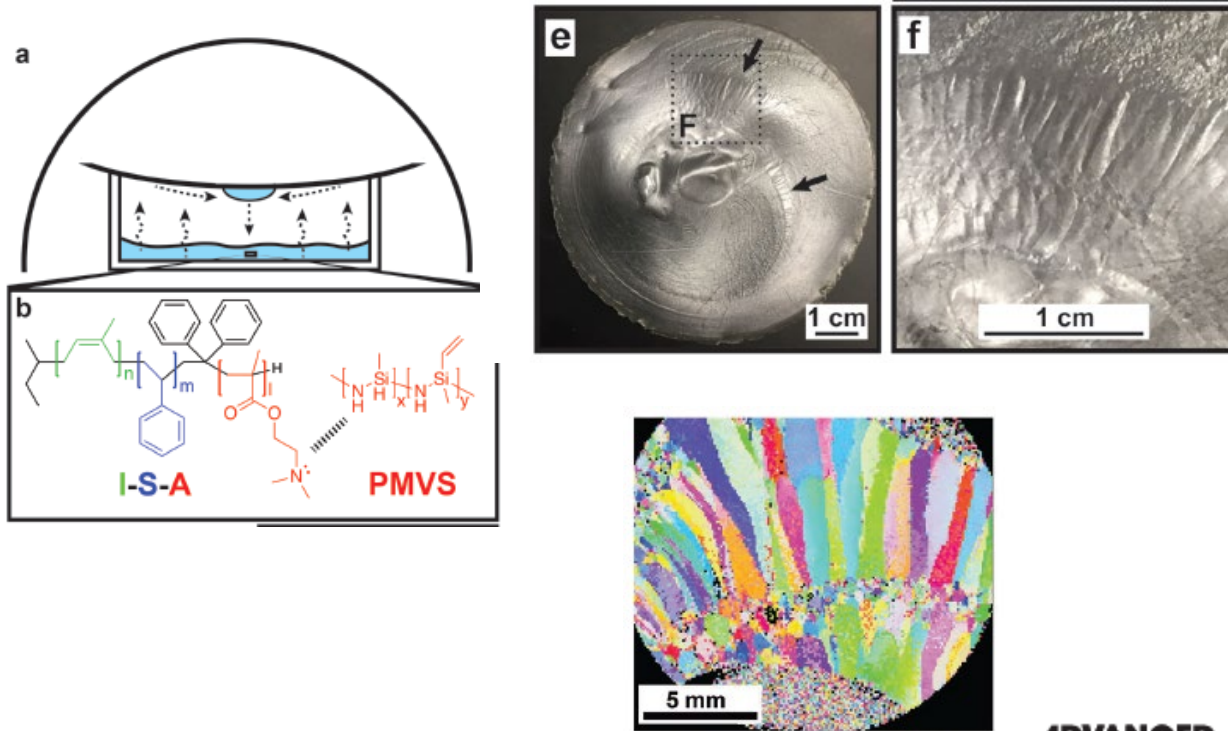


References

- Susca, E. M., Beaucage, P. A., Thedford, R. P., Singer, A., Gruner, S. M., Estroff, L. A., & Wiesner, U. (2019). Preparation of Macroscopic Block-Copolymer-Based Gyroidal Mesoscale Single Crystals by Solvent Evaporation. *Advanced Materials*, *31*(40), 1902565. <https://doi.org/https://doi.org/10.1002/adma.201902565>
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- Dehmel, R., Dolan, J. A., Gu, Y., Wiesner, U., Wilkinson, T. D., Baumberg, J. J., Steiner, U., Wilts, B. D., & Gunkel, I. (2017). Optical Imaging of Large Gyroid Grains in Block Copolymer Templates by Confined Crystallization. *Macromolecules*, *50*(16), 6255–6262. <https://doi.org/10.1021/acs.macromol.7b01528>
- Djeghdi, K., Karpov, D., Abdollahi, S. N., Godlewska, K., Holler, M., Donnelly, C., Yuasa, T., Sai, H., Wiesner, U. B., Steiner, U., Wilts, B. D., Musya, M., Fukami, S., Ohno, H., Diaz, A., Llandro, J., Gunkel, I., (2023). X-ray nanotomography reveals formation of single diamonds by block copolymer self-assembly. arXiv:2304.12027v2. <https://doi.org/10.48550/arXiv.2304.12027>
- Abdelrahman, D., Iseli, R., Musya, M., Jinnai, B., Fukami, S., Yuasa, T., Sai, H., Wiesner, U. B., Saba, M., Wilts, B. D., Steiner, U., Llandro, J., & Gunkel, I. (2023). Directed Self-Assembly of Diamond Networks in Triblock Terpolymer Films on Patterned Substrates. *ACS Applied Materials & Interfaces*, *15*(50), 57981–57991. <https://doi.org/10.1021/acsam.3c10619>



Mesoscale Gyroid Grains 2019: No Control of Size



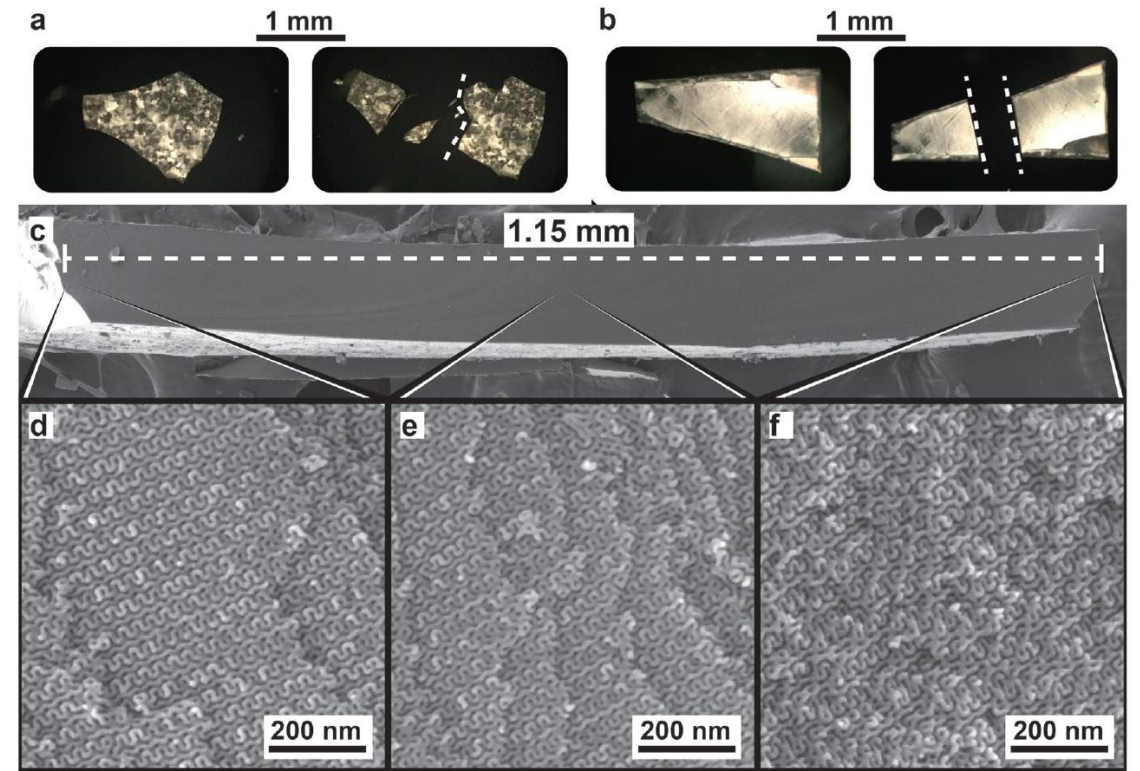
COMMUNICATION

Mesophase Bulk Single Crystals

Preparation of Macroscopic Block-Copolymer-Based Gyroidal Mesoscale Single Crystals by Solvent Evaporation

Ethan M. Susca, Peter A. Beaucage, R. Paxton Thedford, Andrej Singer, Sol M. Gruner, Lara A. Estroff, and Ulrich Wiesner*

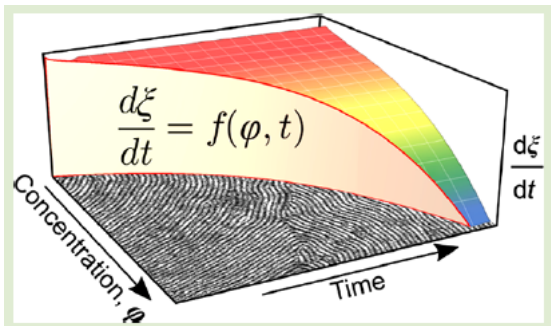
ADVANCED MATERIALS
www.advmat.de



7-24 days of annealing
Grain sizes **7 – 14 mm²**)
Film **thickness 100-300 μm**

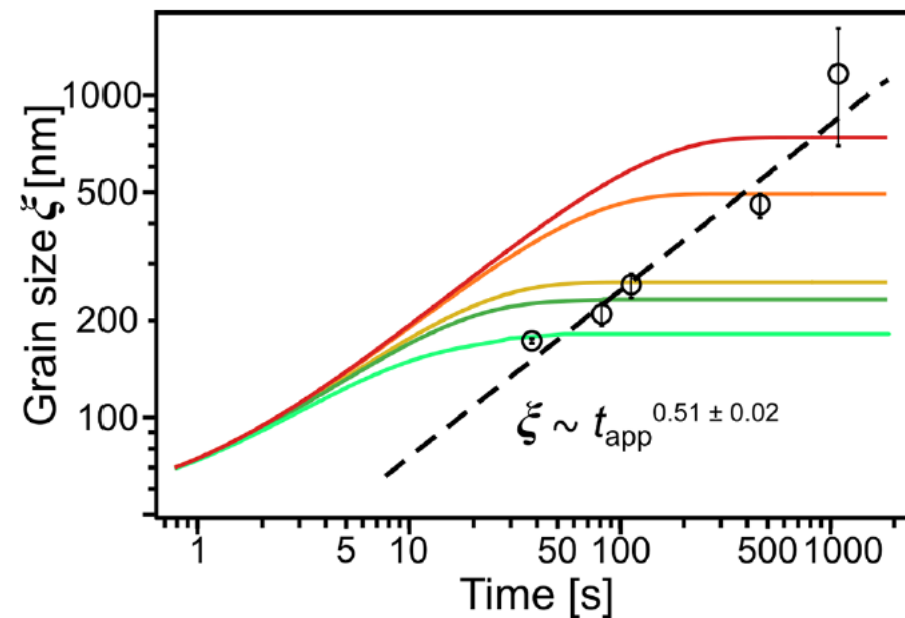


SEA 2022: Controlling Cylindrical Morphologies



The temperature of the chamber was initially increased to rapidly evaporate the solvent and saturate its vapor pressure above the drying sample ... After a certain amount of time, the samples were quenched to completely remove the solvent.

Grain sizes up to 500 nm diameter (about **0.25 μm^2**)
Wetfilm **thickness 400 nm**



ACS **Macro Letters**

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Letter

Pathway-Dependent Grain Coarsening of Block Copolymer Patterns under Controlled Solvent Evaporation

Arkadiusz A. Leniart, Przemyslaw Pula, Robert W. Style, and Pawel W. Majewski*



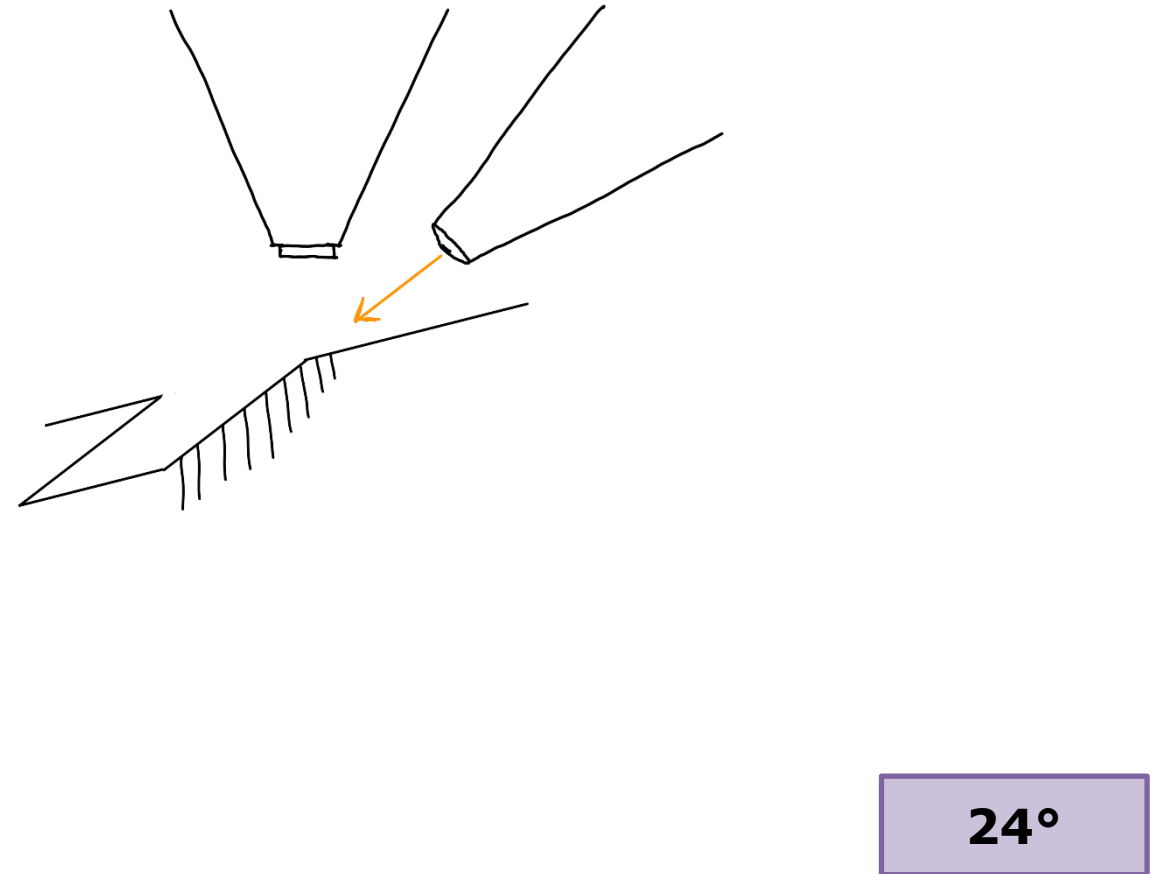
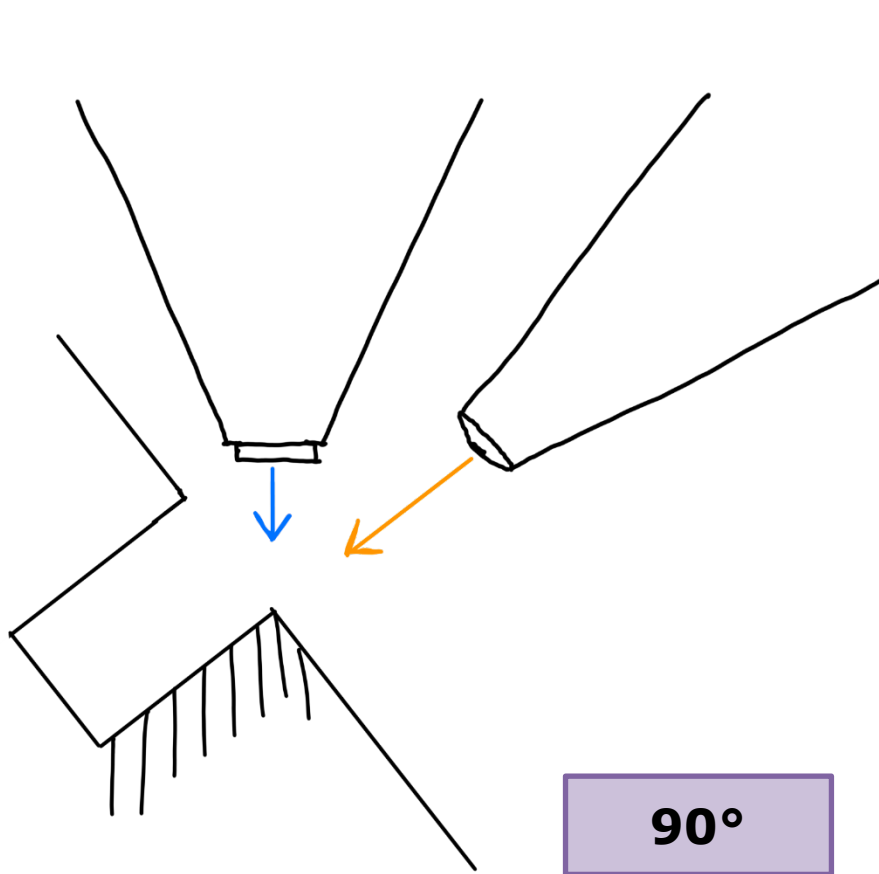
Cite This: *ACS Macro Lett.* 2022, 11, 121–126



Read Online



Method FIB SEM





Method Code – Matching with Ideal Model

