

**Dr. Paweł W. Majewski**  
**Department of Chemistry**  
**University of Warsaw**

**ATTACHMENT 4**  
**INDICATION OF THE SCIENTIFIC ACHIEVEMENT**



Warszawa, 04.15.2019

1. **NAME OF APPLICANT**

Paweł W. Majewski

2. **EDUCATION**

**PhD** Yale University, Chemical Engineering Department, 2013

Thesis title: *"Magnetic Alignment and Charge Transport Improvement in Functional Soft Materials"*

**MPhil, MSc** Yale University, Chemical Engineering, 2009, 2010

**MSc** Molecular Biology, University of Warsaw, 2008

**MSc** Chemistry, University of Warsaw, 2006

3. **EMPLOYMENT**

Since 09.2016, adjunct, Department of Chemistry, University of Warsaw

2013–2016, postdoctoral researcher, Center for Functional Nanomaterials, Brookhaven National Laboratory, USA

2008–2013, teaching/research assistant, Chemical Engineering Department, Yale University

4. **INDICATION OF THE ACHIEVEMENT RESULTING FROM ART. 16 SEC. 2 OF THE ACT OF 14 MARCH 2003 ON ACADEMIC DEGREES AND ACADEMIC TITLE, AND ON DEGREES AND TITLE IN THE FIELD OF FINE ARTS (JOURNAL OF LAWS OF 2017, ITEM 1789)**

a) A series of monothematic publications [H1-H8], entitled:

***Development and characterization of laser-directed block copolymer self-assembly method and its application in the synthesis of ordered arrays of nanomaterials***

b) Publications in the series are listed below with impact factor and number of citations given in square brackets [IF, number of citations], data from Web of Science Core Collection Clarivate Analytics, entry date 04.15.2019:

**H1.** Majewski, P. W.; Yager, K. G. *Millisecond Ordering of Block Copolymer Films via Photothermal Gradients*. ACS Nano 2015, 9 (4), 3896–3906. [13,334; 55]

Chronologically, this is the first publication in the series dedicated to the analysis of physicochemical processes associated with the dynamic laser processing of block copolymers thin films. My contribution to this work consisted, at the pre-experimental stage, in theoretical analysis of heat transport phenomena during laser heating and proposing a concept for further experimental studies. The concept assumed using special low heat thermal conductivity substrates coated with a light absorber layer (later determined to consist of sputtered germanium layer) optimized both for the laser heating application and for surface interactions with polymers. After testing the substrates, I designed and built various mechanical elements of the experimental setup and characterized the main physical parameters influencing self-assembly and long-range ordering of a model block copolymer (optical and thermal profiles, the impact of scanning velocity and number of scanning cycles, degradation limits, etc.). The study demonstrated that this method allows the kinetics of self-assembly of block copolymer domains to be accelerated by more than 1000-fold, which effectively shortens the time of annealing from several hours to a few minutes in comparison with conventional vacuum oven processing. I prepared a series of laser-annealed samples for the analysis of grain growth kinetics as well as a reference series processed in a vacuum oven and characterized them with SEM and GISAXS to compare the kinetics of the self-assembly process in both experiments. I wrote the initial version of the manuscript with illustrations and plots.

I estimate that my quantitative contribution to this manuscript is 65%.

**H2.** Majewski, P. W.; Yager, K. G. *Block Copolymer Response to Photothermal Stress Fields*. Macromolecules 2015, 48 (13), 4591–4598. [5,554; 15]

The soft-shear LZA (SS-LZA) method described in this publication allows obtaining macroscopically ordered (monodomain) specimens of block copolymers thin films. The initial stimulus for this experimental series which led to the development of SS-LZA technique was the long-range ordering of BCP layers observed during my work on the model PS-*b*-PMMA BCP H1 (SI) under creep-flow conditions in films whose mechanical continuity was interrupted. Here, the morphology-aligning bias was shear stress applied to the BCP by the top-coated layer of PDMS elastomer with a high coefficient of thermal expansion. The shear stress was employed in a controllable to give uniaxial directionality to the BCP undergoing laser-induced microphase separation. My contribution to this work was to propose a preliminary research concept and characterize the physical processes accompanying the photothermal shearing of block copolymer thin films. In order to test the applicability of the method, I conducted a series of SS-LZA experiments on block polymers with various chemical composition and mechanical properties, and with different molecular weight. I monitored the efficiency of the process using SEM and GISAXS techniques and participated in the development of a theoretical explanation of the observed differences in the behavior of individual materials. This led to the development of a generalized protocol which allows rapid optimization of SS-LZA parameters for a new BCP system. I participated in the work on the text and illustrations of the publication.

I estimate that my quantitative contribution to this manuscript is 75%.

- H3.** Majewski, P. W.; Rahman, A.; Black, C. T.; Yager, K. G. *Arbitrary Lattice Symmetries via Block Copolymer Nanomeshes*. Nature Communications 2015, 6. [11,329; 52]

In this publication, describing the synthesis of novel metallic nanostructures by self-assembly of BCPs, I developed the sequential laser ordering method allowing fabrication of multilayered inorganic nanomeshes. I also carried out experiments with metallization of block copolymer matrices to obtain substrates covered with metal nanowires arrays, whose electrical conductivity was characterized as a function of the annealing temperature. I performed SEM imaging and GISAXS studies presented in this work. The contribution of individual authors has been described in the published article, in accordance with the requirements of the publisher and is publicly available: „K.G.Y. and P.W.M. devised the fabrication concept, built the annealing apparatus, performed the GISAXS experiments and conducted the data analysis. P.W.M. developed the materials preparation protocols, prepared the experimental samples, and conducted the SEM, optical, and electrical characterizations. C.T.B. and A.R. developed and performed the vapour infiltration methods, and contributed to the electrical and optical characterization. All authors contributed to manuscript preparation.”

I estimate that my quantitative contribution to this manuscript is 60%.

- H4.** Majewski, P. W.; Yager, K. G. *Latent Alignment in Pathway-Dependent Ordering of Block Copolymer Thin Films*. Nano Lett. 2015, 15 (8), 5221–5228. [13,779; 23]

This manuscript reports the critical role of early stages of self-assembly on the further development of BCP morphology. My contribution to this work consisted in developing a research concept and experimental and data-processing procedures. I prepared of a series of BCP samples subjected to ultrafast laser soft-shearing (LZA-SS) inducing latent ordering of block copolymer domains and then characterized the morphology of these materials. I developed a method of visualizing fine morphological details in BCP films at the latent alignment stage. I participated in the development of a semi-quantitative physical model explaining the latent alignment phenomenon. I participated in the preparation of illustrations and writing of the manuscript.

I estimate that my quantitative contribution to this manuscript is 75%.

- H5.** Majewski, P. W.; Yager, K. G. *Reordering Transitions during Annealing of Block Copolymer Cylinder Phases*. Soft Matter 2016, 12 (1), 281–294. [3,889; 20]

This publication is dedicated to the role of kinetic and thermodynamic control in the process of self-assembly of block copolymers. My contribution to this work started with the initial observation of the reorientation phenomenon during the LZA and oven-annealing experiments. Subsequently, I identified a model block copolymer system which, under controlled conditions (optimized

temperature range and film thickness), undergoes a transition from vertically- to horizontally-oriented hexagonally-packed cylinder morphology while conserving the overall film thickness. Afterwards, I carried out a series of microscopic (SEM) and diffraction measurements (GISAXS) to obtain a statistically significant set of images and diffractograms subjected to further analysis and comparison with the developed simulation model. I participated in the preparation of the manuscript.

I estimate that my quantitative contribution to this manuscript is 60%.

- H6.** Majewski, P. W.; Yager, K. G. *Rapid Ordering of Block Copolymer Thin Films*. *Journal of Physics: Condensed Matter* 2016, 28 (40), 403002. [2,649; 28]

It is an extended review publication summarizing the advances in accelerated directed self-assembly of block copolymers. Additionally, there are several chapters with our novel, non-reproduced contribution including a tutorial chapter describing the methods of quantitative characterization of the surface morphology of block copolymers by electron microscopy and X-ray scattering and a chapter where a quantitative comparison of different methods of directed self-assembly was made. We divided the work on the publication by chapters. I wrote chapters 4 and 6 after reviewing and analyzing the publications of other researchers, selecting illustrations and obtaining permission for reproducing other authors' work. We worked together on the introduction and tutorial chapters and on laser-ordering (chapter 7), editing and standardizing the text and editing figures.

I estimate that my quantitative contribution to this manuscript is 50%.

- H7.** Rahman, A.; Majewski, P. W.; Doerk, G.; Yager, K. G.; Black, C., T. *Non-native three-dimensional block copolymer morphologies*. *Nature Communications* 2016, 7, 13988. [12,124; 16]

The contribution of individual authors has been described in the published article, in accordance with the requirements of the publisher and is publicly available: "A.R. and C.T.B. designed the original experiments. A.R. prepared samples, developed the fabrication protocols, characterized with SEM and explored system parameter spaces. P.W.M. and G.D. assisted with refining experimental protocols. K.G.Y. and P.W.M. performed X-ray scattering characterization, and developed image analysis methods. K.G.Y. developed the mechanistic model. C.T.B. and K.G.Y. supervised the work. All authors contributed to the analysis, interpretation and manuscript preparation." In addition, I conducted AFM studies of block copolymer samples after infiltration with the organometallic precursor showing that the infiltration leads to selective swelling of the PMMA domains and formation of topographical "bulges" in these areas. This observation was crucial for the interpretation of morphology of multilayer samples and the influence of layers located below on self-assembly and registration of the upper layers with respect to the underlying layers and the proposed graphoepitaxial model explaining this phenomenon.

I estimate that my quantitative contribution to this manuscript is 35%.

- H8.** Choo, Y.; Majewski, P. W.; Fukuto, M.; Osuji, C. O., Yager, K. G. *Pathway-engineering for highly-aligned block copolymer arrays*. *Nanoscale*, 2018,10, 416-427. [7,233; 3]

This publication is a realization of the research concept originally developed by me and Dr. Yager, related to combining the kinetic (LZA shearing) and thermodynamic control of BCP directed self-assembly in order to obtain monodomain samples of block copolymers composed of vertically-oriented hexagonally-packed cylinders. I developed an initial experimental plan for this work and carried out preliminary tests, identifying the RTP (Rapid Thermal Processing) method following the SS-LZA ordering as an optimal tool to achieve the final, thermodynamically-prescribed morphology with uniquely defined hexagonal lattice orientation. I participated in SAXS and GISAXS transmission studies of the pre-sheared samples and analysis of the data. I also participated in preparation and edition of the manuscript.

I estimate that my quantitative contribution to this manuscript is 40%.

## **c) description of scientific/artistic merits of the submitted work and their perspective applications**

### Abstract and summary

Controlling long-range ordering in block copolymers (BCP) is not a simple task. Due to the low enthalpic cost of introducing structural defects in these materials, BCP morphologies formed during spontaneous self-assembly generally lack long-range order. An additional difficulty in processing these materials is the long duration of ordering associated with their high viscosity and very slow kinetics of the growth of ordered domains. During my post-doctoral research at the Brookhaven National Laboratory, I developed a method of directing self-assembly of block copolymers thin films using laser light. This directed self-assembly (DSA) technique turned out to be much more efficient than conventional vacuum annealing of BCPs and also easily adaptable to processing various types of block copolymers. A variant of the technique, in which laser irradiation is coupled with soft-shearing of top surface of BCP films, enables efficient production of macroscopically-ordered block copolymer films, which in turn are used for templated synthesis of inorganic nanomaterials. This synthetic approach opens new perspectives for functional surface coatings e.g., transparent electrodes, plasmonic materials or sensors.

I continue research in block copolymers and other soft self-assembling systems after joining the Faculty of Chemistry of the University of Warsaw in 2016. I am a leader of a research group, funded thanks to the financial support received from the Foundation for Polish Science (FNP) and National Science Centre (NCN). Currently, apart from further basic BCP research and advancing the laser-annealing technique itself, we implement new scientific ideas related to the use of ordered diblock polymers as templates for ordering other organic nanostructures (nanotubes, nanoribbons) as well as the synthesis of ordered layers of inorganic nanomaterials with potential use as chemical sensors. One of the group's recent achievements is the development and construction of a miniaturized laser processing setup compatible with synchrotron beamline's infrastructure that enables structural investigation of materials using grazing incidence X-ray scattering (GISAXS) *in situ* during laser processing. These experiments should help elucidating the role of early stages of the self-assembly process difficult to investigate with other methods.

The scientific achievement indicated by me is a series of monothematic publications related to the laser annealing of block copolymers. The series consists of the following: a record of the discovery and description of the phenomenon (H1), a detailed characterization of processing parameters and development of a model explaining the observed phenomena (H2, H4, H5), and finally, a demonstration of the use of the method (H3, H7, H8). In particular, an important applied aspect of the work is the fabrication of nanostructured coatings composed of highly ordered nanowires obtained by matrix synthesis from thin layers of block copolymers subjected to photothermal treatment. The photothermal method allows for quick preparation of individual polymer layers being components of complex multilayer systems. In one of the publications (H3), exemplary applications of this type of nanostructured coatings are presented. This work, similarly to publication (H7), presents methods for obtaining coatings composed of several layers of diblock copolymers that yield nanomaterials with much more complex morphologies than the ones obtained as a result of self-assembly of single-layered BCPs.

The H6 publication is a review work summarizing the state of research in accelerated methods of directed self-assembly of block copolymers. In addition to demonstrating the state of the art in this field, this work quantitatively compares the performance of different techniques of DSA and includes a tutorial section for researchers beginning research BCP thin films. The tutorial describes quantitative methods of analysis of BCPs' morphology and self-assembly kinetics characterization including scanning electron microscopy (SEM) and grazing incidence small angle X-ray scattering (GISAXS) techniques.

## Short introduction and motivation

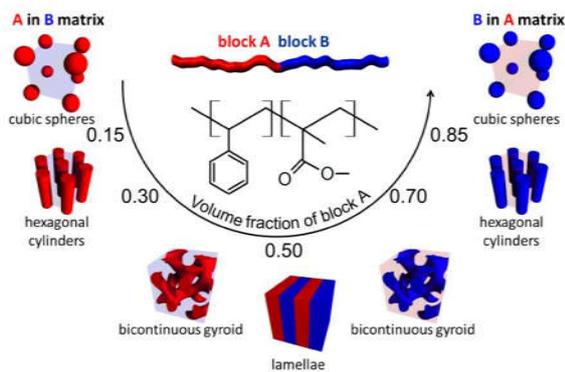


Figure. 1 Equilibrium morphologies of coil-coil diblock copolymers

Block copolymers are an elegant self-assembly motif, in which two chemically distinct segments of a macromolecule microphase-separate into a nanoscale morphology with well-defined periodic architecture. For diblock copolymers, the most readily accessible morphologies are cubic spheres, hexagonal cylinders, or alternating lamellae [1,2] (Fig. 1). Owing to the ease with which nanoscale order can be generated and convenience of processing (usually solution-based), these materials are promising for a host of applications.[3] In these applications BCP thin films can be used directly as a functional component of the device e.g., as ion-conducting membrane [4, 5, 6], or as lithographic pattern[7], or can be utilized as a matrix for nanomaterials synthesis and surface patterning.[8,9] BCP nanopatterns can be converted into inorganic replicas, giving rise to plasmonic structures,[10] gas sensing nanowires,[11] or light polarizers [12]. Nanostructured metallic layers strongly influence optical properties of coated surfaces, enabling “light-management” in thin-film devices, e.g., to improve solar energy harvesting[13]. Electrical properties of nanostructured films are relevant in applications such as flexible transparent electrodes[14], capacitive sensing,[15] triboelectric energy harvesting,[16] or gas sensors.[17] Surface topography influences wetting properties, enabling, e.g., super-hydrophobic coatings.[18]

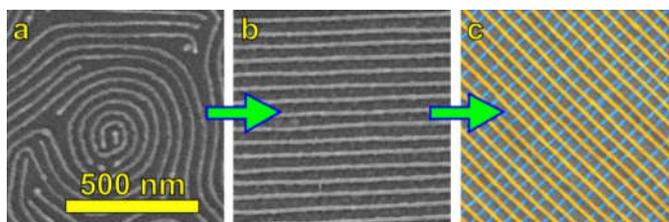


Figure. 2 Directed self-assembly of BCPs: a) spontaneously formed defected structure, b) single-layered aligned morphology, c) double-layered aligned nanostructures derived from a BCP matrix.

## Detailed description of publication series

The first of the series of works (H1), *Millisecond Ordering of Block Copolymer Films via Photothermal Gradients*, describes the method of directed self-organization of block copolymers, in which BCPs are ordered using a line-focused laser beam (Laser Zone Annealing, LZA). The publication outlines the construction of a system for laser annealing of thin layers of block copolymers and the physical phenomena accompanying this process.

The name Laser Zone Annealing assigned to this technique refers to other techniques of zone annealing of materials, including to the CZA (*Cold Zone Annealing*) method developed by the group of prof. Karim [19, 20] and the techniques of localized heating of polymeric materials during extrusion processing, which gives the chains in crystalline and semi-crystalline materials a spatial order[21]. The hot extrusion methods[22], described by the term *Hot Zone Annealing*, are distinguished from the CZA technique by the fact that the processed materials are melted to the isotropic phase. In the case of the LZA method described here, as in the case of the CZA, maximum temperatures used are often significantly higher than the glass transition temperature ( $T_g$ ) but never exceed the order-disorder transition temperature ( $T_{ODT}$ ). The full name of this technique could therefore be *Laser Cold-Zone Annealing*, and would be somewhat confusing taking into account that the temperatures transiently reached by the polymer film might exceed 500 °C.

The LZA method consists in sweeping the focused laser beam (532 nm, 3W) over the surface of germanium-coated glass substrate (Ge acts as a light-absorbing layer) covered by a thin layer of block copolymer (Fig. 3a). The beam, thanks to the use of cylindrical lenses, has the shape of a narrow line, approx. 10 mm long and 10  $\mu$ m wide, which allows simultaneous ordering of samples of considerable width, in contrast to the work of other researchers who used point-focused light for processing small area specimens,

often using a microscope for focusing the light [23, 24]. As shown experimentally, the LZA method allows ultra-fast self-assembly of BCP domains. For a typical thermal profile width ( $<100 \mu\text{m}$ ) and laser line scan speed of  $1000 \mu\text{m/s}$ , the method allows to obtain ordered BCP morphologies in less than 100 ms. In the manuscript, we presented a quantitative comparison of grain growth kinetics in a model BCP system (cylinder-forming polystyrene-*b*-polymethacrylate) between conventional annealing in a vacuum oven and LZA processing. We demonstrated more than 1000-fold acceleration of self-assembly kinetics in the case of laser annealing (here, reported as the shortening of time needed for self-assembly and growth of uniformly-ordered domains to a certain aerial size) (Fig. 3b) It should be emphasized that at this stage of work no preferential direction of domains' growth was observed. The acceleration of grain-growth kinetics in the presence of thermal gradients was observed by other researchers, e.g. in the cold-zone annealing (CZA) experiments. Berry and co-workers reported a 10-fold increase in the domain growth rate using linear temperature gradients of the order of  $10\text{-}70^\circ\text{C/mm}$  [19]. In the H1 publication (supplementary materials), we postulated that the effect of accelerated growth of BCP domains, observed both for cylindrical domains in horizontal and vertical orientation, can be attributed to the thermophoretic migration of defects towards the hotter zone of the gradient and their concentration therein accelerating the elimination of defects by annihilation of pairs with opposite polarity. It should be stipulated that other factors also influence the growth rate of domains in block copolymer systems, including the thickness of the film and the type of substrate chosen, and obtaining and comparing kinetic parameters requires a lot of experimental skill and the use of an appropriate method of grain size analysis. The automated analysis of spatial correlation of domains in SEM images developed for the needs of H1 work is an objective and universal tool which excludes human errors and other biases frequent in "manual" domain size calculations. This method involves the identification of microdomains and then assigning local spatial orientation vectors to them and conducting their correlation analysis. It can be universally used to analyze the size and orientation of domains with other symmetries e.g. hexagonal lattices. The advantage of the method is its high sensitivity to structural defects including, for example, undulations of the line-patterns and other imperfections of the image, which means that the obtained spatial correlation values are very conservative and typically lower than those obtained by manual methods.

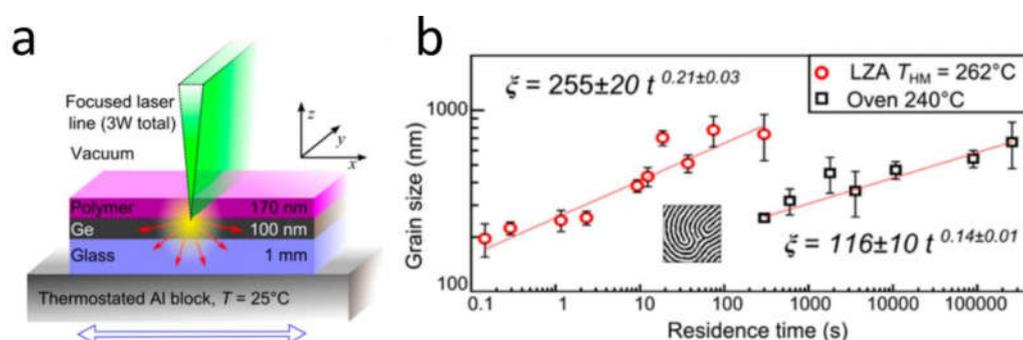


Figure 3. LZA method a) scheme of the laser system for heating the thin layers of the block copolymer, b) accelerating the growth process of the BCP macro-domain using this method (Graphics taken from H1)

In addition to a strictly scientific contribution to explanation of observed phenomena and finding key physical parameters affecting the process of LZA, my contribution to the study also involved solving several engineering difficulties. One of them was finding suitable substrates compatible with general BCP-processing routines that would enable indirect heating of the BCP films (typical block copolymers do not absorb 532 nm radiation). Standard silicon substrates are very efficient heat conductors preventing local heating at optical power densities available in this study, while the organic dyes that I tried to blend with polymers turned out to be unstable due to sublimation, boiling, photo-bleaching or, thermal degradation under intense illumination. Lesser stability problems were found in thin, strongly absorbing inorganic coatings such as PbS or CuO/Cu<sub>2</sub>O, but there are several problems related to their roughness and difficulties in obtaining layers of controlled thickness and chemical stability. The sputter-coated Ge layers that I proposed possess both good thermal and chemical stability (under non-oxidizing processing conditions), but most importantly can be

deposited on glass substrates in a controlled manner assuring good reproducibility of the coating thickness and thus reproducibility of temperature fields used in LZA. Ge also displays significant chemical similarity with commonly used silicon substrates, which facilitates direct applicability of coating protocols and processing tools used in BCP research.

An additional experimental challenge was the assessment of very steep temperature profiles on the surface of BCP substrates under exposure to laser beam. The measurements were further compared with the results obtained by simulating the process (finite element simulation) as well as with the theoretical solution of the problem of heat transport in this geometry. The method proposed by me for the reconstruction of thermal fields in thin layers heated by laser is based on the use of thin coatings of a reference substance with a well-known melting point and thickness selected to have a similar anti-reflective coating (ARC) properties as the polymer films used in the study. The reference substance should also not sublime near the melting point temperature. In the case of LZA, a series of measurements of the “melt marks” (melt marks analysis) for two reference substances - stearic acid (SA,  $T_m = 70\text{ }^\circ\text{C}$ ) and tetrabutylammonium hexafluorophosphate (TBA HFP,  $T_m = 245\text{ }^\circ\text{C}$ ) – was used to reproduce the confirm theoretically-predicted and simulated profiles.

Due to the very large number of parameters affecting the process of BCP annealing e.g., beam focus, laser power, sweep velocity and number of beam sweeping cycles, a major challenge in this work was to identify key process control parameters allowing optimization of the method. The method of LZA control-parameters analysis implemented here was based on simultaneous screening the influence of two orthogonal process parameters in logarithmic increments e.g., the sweep velocity and number of cycles and plotting the obtained results e.g., domain size derived from SEM image analysis as two-dimensional matrices.

The observation of macroscopic directional ordering of domains in polymer films subjected to a very slow sweep of the laser line at high optical power (H1 SI) had a critical role for the whole research cycle. The domains' ordering under these conditions was almost always accompanied by local (band-like) thermal degradation of polymer films and disruption of the mechanical continuity of the film causing creep flow of the material. The identification of stresses related to viscous flow during laser processing of the film as a directional alignment stimulus was originally confirmed by an experiment in which the continuity of the layers was mechanically broken before the LZA experiment and then gave rise to experiments in which the source of shear stress was introduced as an additional element of the experiment, ultimately leading to the development of the LZA Soft-Shear method.

The LZA Soft-Shear (SS-LZA) technique is described in detail in the publication H2, *Block Copolymer Response to Photothermal Stress Fields*. The method employs a significant difference in the thermal expansion coefficient of an inorganic substrate (BK7 glass or silica covered with a thin layer of germanium) onto which a block copolymer layer is applied and a transparent elastomer (cross-linked poly (dimethylsiloxane), PDMS) coated on top of the BCP. The PDMS layer has a macroscopic thickness (about 0.5 - 1 mm) and does not absorb laser light, while being heated by the diffusion of heat from the bottom layers. Differential thermal expansion and shear stresses arising on the boundary of polymer substrate layers coupled with the movement of laser lead to strong dynamic stresses and microscopic shear-fields acting in the direction of the laser line sweep Figure 4 depicts the result of numerical simulation of strain, shear rate and stress fields based on experimentally-determined temperature distribution in the material processed at typical SS-LZA conditions.

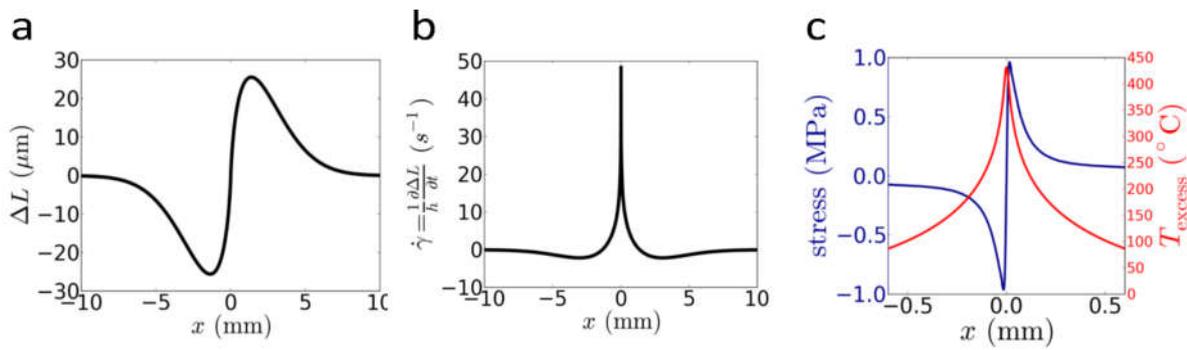


Figure 4. a) Estimate of local strain profile in the elastomer layer during SS-LZA, b) estimate of shear rate during SS-LZA. The shear rate is calculated by taking the derivative of Figure 4a, and equating position ( $x$ ) with time ( $t$ ) using a typical laser-sweep velocity of  $v_s = 320 \mu\text{m/s}$ . c) Plot of the stress at the boundary between the two layers (i.e. that which would be experienced by the BCP film), along with the corresponding temperature (Source of graphics: SI of H2)

I extended the scope of SS-LZA experiment to six different diblock copolymers with cylindrical morphology various composition of minority block and polystyrene majority block (approx.. 65% of PS volume fraction) with approximately constant total molecular weight  $M_n \approx 50 \text{ kg/mol}$ . The minority phase was formed by poly(methyl methacrylate) (PMMA), poly(2-vinylpyridine) (P2VP), poly(ethylene oxide) (PEO), poly(isoprene) (PI) and poly(dimethylsiloxane) (PDMS). The main finding of this experimental study, besides the refinement of the SS-LZA ordering protocol, was the identification of significant differences in nano-mechanical response to photothermal shear stimuli between the polymers of different chemical makeup. The differences in the degree of alignment resulting from different response of materials to photothermal shearing rates are shown in Figure 5a, which presents the GISAXS diffractograms for each type of BCP film measured after a series of SS-LZA experiments. In the presented series every sample was laser-processed for the same duration of time but at a varying laser sweep velocity and for a different number of sweep cycles. As a result, two types of BCP systems were identified. In materials such as PS-*b*-PMMA and PS-*b*-PEO the degree of ordering and alignment depended little on the shear rate applied in SS-LZA. Conversely, PS-*b*-P2VP and PS-*b*-PI BCP responded to photothermal shearing only after the shearing rate exceeded certain threshold value. As a possible source of this effect, the influence of glass transition temperature, macroscopic mechanical parameters such as shear modulus and microscopic parameters such as relaxation time of the polymer segments ( $t_a$ ) and relaxation time at the level of morphology were considered. By analyzing the source data, we have identified the relaxation time at the morphology level (fluctuation relaxation time)[25] as defining the response of the materials in this study (Figure 5b and 5c). Block copolymers, in which the minority block relaxes very quickly, are susceptible to this type of ordering only after using very rapid thermo-mechanical stimuli. The SS-LZA conditions and the characteristic relaxation times of the polymers studied are shown in Figure 5s. This graph provides useful hints when planning SS-LZA experiments using previously-untested block copolymers.

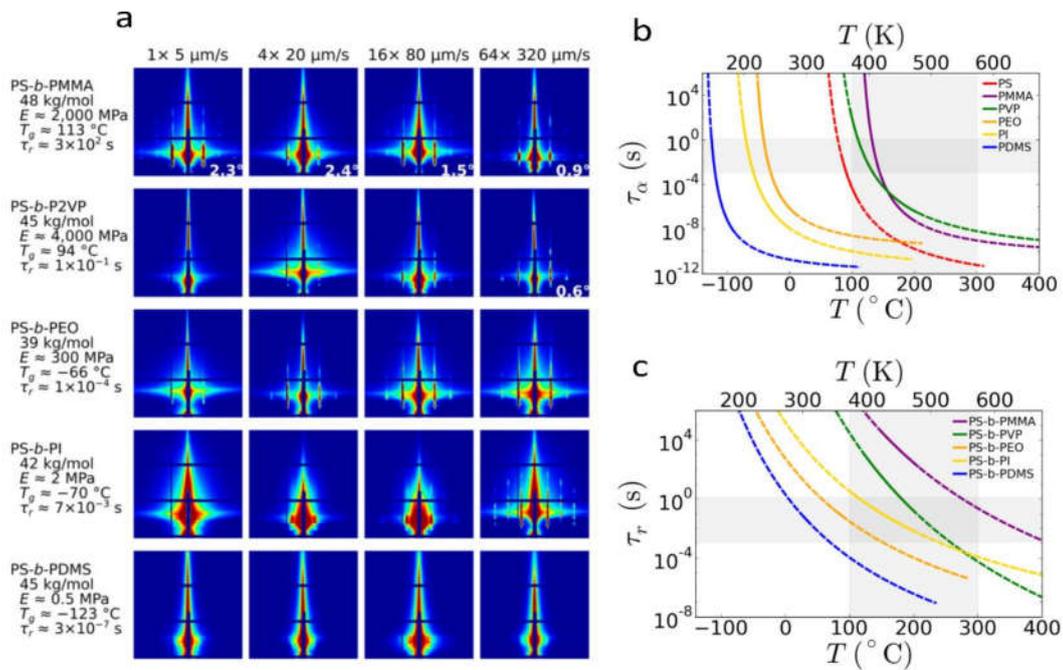


Figure 5. a) GISAXS diffractograms of various BCPs after SS-LZA processing b) temperature-dependent segmental relaxation times,  $t_\alpha$  for homopolymers corresponding to the BCP components used in the study c) temperature-dependent BCP morphology relaxation times; time scales and temperature range relevant to SS-LZA processing are marked as shaded regions (Plots source: H2, S1)

In the H3 publication, *Arbitrary Lattice Symmetries via Block Copolymer Nanomeshes*, the SS-LZA method was applied in preparation of macroscopically aligned diblock polystyrene-*b*-poly(2-vinylpyridine) copolymer homologs which were subsequently used for the synthesis of highly ordered single- and multilayer arrays of inorganic nanowires. My contribution to this work consisted in proposing a fabrication concept and developing a protocol for obtaining multilayered BCP-derived structures with novel morphology. This step-by-step approach relies on successive steps of 1) coating the substrate with the polymer, 2) SS-LZA ordering and 3) conversion of the polymer matrix to the inorganic replica. The conversion can be accomplished either by selective complexation of aqueous metallic precursors delivered in the liquid phase by pyridine residues in BCP yielding Pt, Pd, Rh, Au metallic nanostructures [26, 27] or by gaseous precursors of metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}_2$ ) [28, 29]. At the end of the cycle, the etching of the polymer matrix with oxygen plasma (4) allows immobilizing BCP-templated layer of nanomaterial before coating the next BCP film and repeating the laser annealing process. Because this method allows independent control of the orientation of BCP domains during each of the deposition/alignment cycles, it allows realization of nanomaterial morphologies not accessible for spontaneous BCP self-assembly. For example, one can prepare double-layered nanolattices consisting of rhombuses and parallelograms with arbitrarily-controlled angle of intersection of the lattice vectors. In this publication this method was also used for ordering of triple-layered systems leading to the formation of hexagonal lattices (Figure 6). We have also described the synthesis of nanolattices composed of nanowires of various composition, including bi-metallic and metal-metal oxide systems.

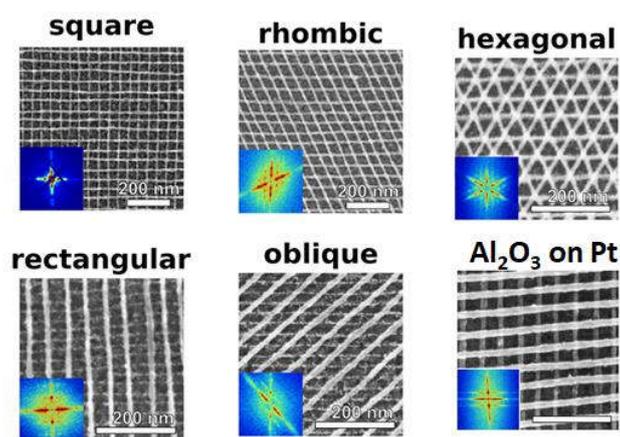


Figure 6. Metallic nanomeshes synthesized using layered BCP templates aligned by SS-LZA method. (Adapted from H3)

As demonstrated in the publication H3, the SS-LZA method can be used to synthesize single-layered dichroic arrays of noble metal nanowires and multilayered nanowire conductive coating. In contrast to the observations by other authors investigating the electrical conductivity of platinum nanowires obtained by PS-*b*-P2VP complexation [25], we observed only negligible electrical conductivity values in the metallic nanowire arrays after ashing of BCP template if no further treatment was used. The conductivity of the wires increases by several orders of magnitude, approaching the values characteristic of bulk metal, only after partial sintering and reduction of nanowires porosity at high temperature, what indicates an important role of crystal lattice defects in the conductivity of nanomaterials derived from BCP template. My contribution was to propose and conduct measurements of the electrical conductivity of the prepared nanowire arrays as a function of post-synthesis annealing treatment performed using the Rapid Thermal Processing technique. An important difficulty to overcome in this process was to find a suitable protective coating (silicon nitride) for germanium which otherwise oxidizes at high temperatures damaging the supported nanowires. Single-layered arrays of metallic nanowires displayed a strong anisotropy of electrical conductivity ( $\sigma_{\text{parallel}}/\sigma_{\text{perpendicular}} > 1000$ ) and (after gentle removal of the germanium layer) linear dichroism in the range 400-450 nm of about 0.7. Two-layered nanomeshes composed of nanowires forming a square lattice showed no anisotropy of electrical conductivity and, as a result of 2D nature of the lattice, their conductivity is only weakly susceptible to the presence of micro and macroscopic defects in the array. Understandably, the higher conductivity of the double-layered structures is accompanied by a drop in light transmission coefficient regardless of the mutual orientation of the polarization plane and the grid axes of the nanowires.

The publication *Latent Alignment in Pathway-Dependent Ordering of Block Copolymer Thin Films* (H4) is a continuation of the basic research in physics of BCP laser-directed self-assembly. It describes an interesting phenomenon of the occurrence of the "latent order" in BCP films subject to the very rapid photothermal shearing. I have shown experimentally that even a single SS-LZA sweep of cylinder-forming PS-*b*-PMMA sample at a velocity of 1.28 mm/s (effective local ordering time of approx. 65 ms) induces long-range ordering in the sample non-apparent without further development steps. The monodomain ordering develops if the sample is subjected to conventional isotropic heating (as well as annealing LZA without shear component). Despite attempts, we have not been able to find evidence of structural anisotropy in the GISAXS patterns of specimens exhibiting latent order processed at the fastest shear rates. However, a very small anisotropy of the morphology of the surface layers in SEM images was observed using a specially developed method of selective etching of PMMA chains with ultraviolet radiation and oxygen plasma followed by Fourier filtering of the micrographs. These observations indicate a deterministic effects of the early stages of BCP domain nucleation (i.e., ordering of small structural units without formation of the extended domains) on the overall pathway of the self-assembly. It is astonishing how small a structural anisotropy in the BCP film can be at those early stages, to further lead to formation of a strongly anisotropic morphology over entire area of the sample. The conclusions from this work were inspiration for continuation of research elucidating the role of DSA pathway and the means of controlling it (H5 and H7). They allowed the creation of a semi-

quantitative model showing the progress of self-assembly of the copolymer expressed as the minimization of Gibbs free energy of the system as a function of microphase separation (formation of the boundary between chain fragments that belong to the distinct BCP blocks) and the progress of (macro)domains growth (Figure 7).

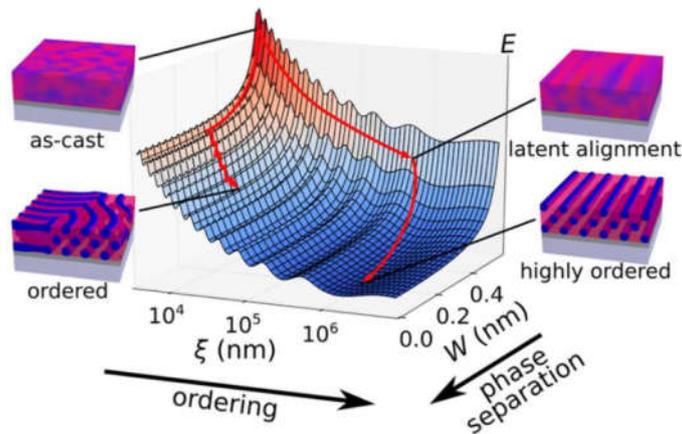


Figure 7. Semi-quantitative model used to explain the latent alignment effect. Ordering proceeds along two axes: phase-separation of the two BCP constituents (characterized by interfacial width  $W$ ) and ordering of the material through defect annihilation and thus growth of domain size ( $\xi$ ). (Reproduced from H4)

In the publication H5, *Reordering Transitions during Annealing of Block Copolymer Cylinder Phases*, we presented a quantitative analysis of the morphological transition consisting in the reorientation of cylindrical BCP domains during laser heating. During this type of transition, the BCP morphology consisting of vertical PMMA cylinders present initially in the annealed films (kinetically controlled morphology) is gradual replaced by a morphology composed of horizontally-oriented cylinders (thermodynamically preferred due to the favorable interaction between the microdomains of one type and the substrate) while maintaining a constant layer thickness. Our initial interest in this process stemmed from my experimental observations that under certain conditions, such a transition leads to the growth of horizontally oriented domains exhibiting an anisotropic structure (elongated in the transverse direction to the long axis of the cylinders). In the paper, we presented a quantitative analysis of this process using SEM images and GISAXS diffraction pattern, obtaining the rate constants of the reorientation process as well as the activation energy using the Arrhenius model. The publication also presented the results of simulation of the reorientation process using a Monte-Carlo simulation model developed by Dr. Yager. The simulation results confirmed the grain anisotropy observation and helped understanding the anisotropic expansion of horizontally-aligned cylinders.

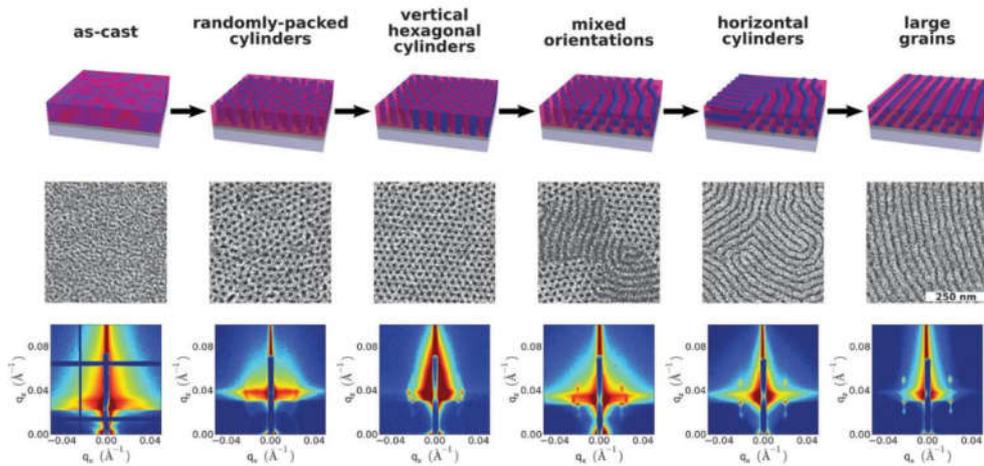


Figure 8. Reorientation transition in the cylinder-forming PS-b-PMMA ( $M_n = 48 \text{ kg/mol}$ ,  $t = 170 \text{ nm}$ ) (Adapted from H5)

The publication H6, *Rapid Ordering of Block Copolymer Thin Films*, is primarily a review of the accelerated directed self-assembly techniques used for block copolymer processing. However, motivated by the lack of comprehensive resource describing quantitative tools used in BCP research we supplemented it with new content of our authorship by adding chapters that are a tutorial on quantitative analysis of the morphology of thin films of block copolymers by means of microscopic imaging (SEM, TEM, AFM) and X-ray scattering (SAXS, GISAXS). An additional element of novelty is the quantitative comparison of performance of various methods of directed BCP self-assembly described in individual chapters and combined within a single grain-growth kinetics plot (Figure 9). Obtaining these data and comparing them turned out to be a big challenge due to the small availability of published quantitative data (some data were obtained through personal correspondence with authors) and major differences in the analysis and reporting methodology. This work is an attempt to unify and summarize these results, it can also be used as a benchmark for the newly-developed DSA methods.

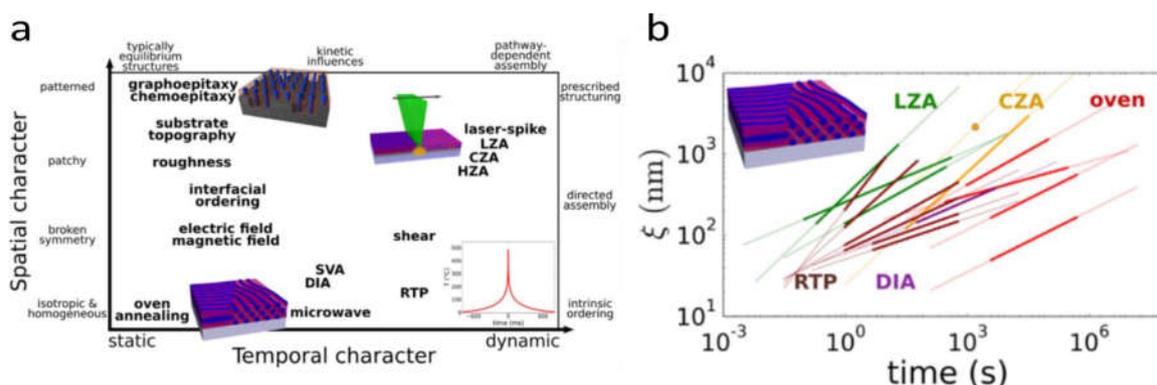


Figure 9. a) Qualitative classification of various DSA methods used in BCP processing based on their spatio-temporal character. b) Quantitative comparison of BCP processing methods) (Source of graphics: H6)

The publication H7, *Non-native three-dimensional block copolymers*, is a continuation of work on obtaining complex surface nanostructures using multilayer systems built of block copolymers. The method presented here consists in immobilizing deposited and annealed block copolymer layers with organometallic precursors vapors interacting with polar BCP residues (Lewis acid-base pair formation) introduced via infiltration from the gas phase. It was developed as an alternative to the method of subsequent layering and metallization of the layers described in publication (H3). In contrast to the previously proposed method, it does not require removing the polymer matrix before applying new polymer layers. The manuscript describes the morphology of several dozen bilayer and three-layered systems composed of PS-*b*-PMMA homologs with cylindrical and lamellar morphology. Prior to deposition on each BCPs layer a thin neutral-brush layer of random PS-PMMA copolymer is grafted onto the surface to ensure "neutral wetting" conditions i.e., adjusting substrate's surface energy by neutralizing preferential interactions of one of the blocks with the substrate to obtain vertically-aligned morphologies. As part of this research, I performed a series of X-ray measurements: GISAXS and SAXS on two-layer samples, analysis and interpretation of the collected data. These measurements were complementary to the SEM analysis carried out, as they allowed to determine the structure of bilayer systems before removal (plasma etching) of organic material. In addition, in contrast to high-magnification microscopic imaging, diffraction techniques, in particular GISAXS, allow collecting global information about macroscopic regions of the sample carrying high statistical weight associated with the large area of the probed surface. In the case of morphologies that are difficult to interpret in the case of samples lacking the directional

ordering, I made the analysis of samples after ordering the first layer by the LZA method.

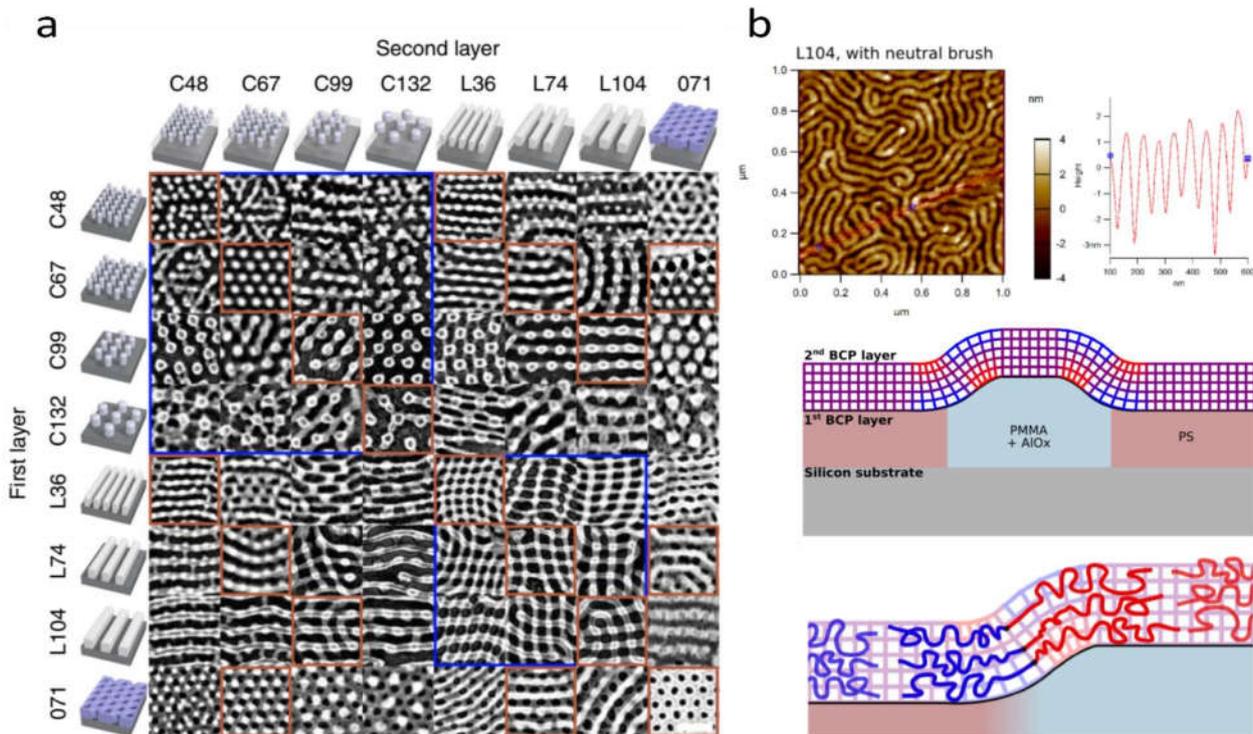


Figure 10. a) Double-layered nanostructures b) mechanism of graphoepitaxial registration of BCP domain boundaries between the top and bottom layers b) (Graphics from H7)

In addition, I helped elucidating the mechanism of interaction and spatial registration of domains in the adjacent stacked layers. (both grapho- and chemoepitaxial effects were initially considered as plausible explanation for the observed effects). The mechanism of overlaying boundary domains in the top layer above the domain boundaries of the lower layer is based on minimizing the energy of stretching and compression of the upper layer polymer chains on the PMMA region protrusions in the lower layer after swelling with the organometallic precursor and water ( $\text{Al}_2\text{O}_3$ ). I confirmed the presence such protrusions located directly above the infused PMMA domains experimentally by performing AFM and ellipsometric measurements of copolymer samples treated with organic metal precursor (trimethylaluminum) and water vapor delivered to the BCP in the Sequential Infiltration Synthesis process[28].

#### Recent advances in laser-directed self-assembly research

Currently, as a leader of the First Team project "*Innovative Nanostructured Functional Materials by Combinatorial Methods of Directed Self-Assembly of Block Copolymers*" awarded by the Foundation for Polish Science, I continue my research focused on directed self-assembly of block copolymers. In particular, our team working at the Department of Chemistry of the University of Warsaw is further advancing photothermal methods of BCP annealing and working on broadening the repository of chemical methods of BCP conversion to inorganic nanomaterials. Our latest achievements include the development of a laser technique for heating copolymer films coated on standard silicon substrates with use of a compact optical system utilizing a high power laser (Figure 11a). Silicon wafers being the "gold standard" in the technology of electronic materials, eliminate the need for specialized substrates coated with light absorbers e.g, graphene- [30] or  $\text{Si}_3\text{N}_4$ -germanium-coated glass which are very laborious in preparation and require specialized tools for preparation. In addition, the proposed method allows quick ordering of very large areas of block copolymer films enabling larger-scale patterning and development of other BCP processing methods e.g., transferring of ordered BCP onto corrugated substrates (Figure 11b). The result are described in details in the manuscript Leniart, A.; Sikiewicz, A.; Puła, P; Majewski, P, W, *Laser-Directed Self-Assembly of Block Copolymers on Silicon Substrates* (in preparation).

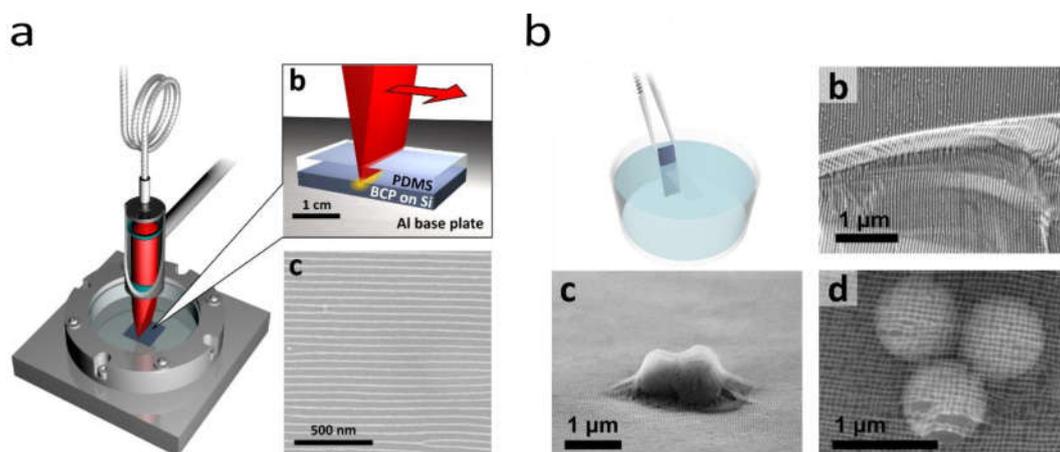


Figure 11. a) Photothermal annealing of BCP on large area Si substrates using compact laser-focusing head. b) Block copolymer layers processed in the annealer after the transfer and conversion to inorganic nanowire arrays.

My team is also conducting a study of non-equilibrium morphologies formation in block copolymer thin films at early stages of self-assembly conducting a research project under a proposal which was granted with measurement time at the Complex Matter Scattering (CMS) beamline at the National Synchrotron Light Source. As a part of the proposal, we conduct research on the early stages of self-organization of block copolymers under highly non-equilibrium conditions. For this purpose, we have developed a prototype version of the laser annealer compatible with GISAXS/GIWAXS synchrotron measurements geometry allowing *in situ* observations of laser-driven self-assembly. This set is a major step towards better understanding the LZA process, as it allows measurements of the structure evolution of materials subjected to laser heating in real time as well as autonomous control of the sample annealing process by means of feedback signals from continuous analysis of diffractograms.

##### 5. Short description of other scientific achievements (for the complete list see Attachment 5).

During my doctoral studies at Yale University, I studied magnetic alignment of soft self-assembling materials focusing on lyotropic liquid crystals (LLC) and block copolymers. One of my main achievements from this period is elucidation of the mechanisms of magnetic alignment in BCP and LCC system of various diamagnetic susceptibility anisotropy subjected to static and rotating magnetic fields (Publications M3-M5, M13 and M15). The alignment experiments were performed utilizing a custom-built setup consisting of small angle X-ray scattering (SAXS) diffractometer equipped with a superconducting 6T electromagnet allowing for *in situ* studies in the transmission geometry. In my work I analyzed both the behavior of magnetically uniaxial and magnetically degenerate systems. The former align along uniquely defined direction in the field while the latter form degenerately-aligned morphologies known as 2D powders. Spatial degeneracy of magnetic alignment in such systems can be removed by controlled rotation of samples about an axis perpendicular to the field (with constant X-ray data acquisition) using the special rotational attachment that I constructed (Publications M3-M5). My further work was aimed at characterizing quantitative relation between the direction and the degree of internal structure ordering in heterogeneous materials (BCPs and LLC with lamellar or cylindrical morphology) and their transport properties, in particular the ionic conductivity. The described research led to a number of scientific discoveries related to the impact of strong magnetic fields on block copolymers (including M4, M9, M15, M16, D1, D3 and D4) and lyotropic liquid crystal systems composed of nonionic surfactants (M3, M5). In my opinion, the two most important publications in this cycle are M6 and M13, in which we demonstrated a strong relationship between the magnetically ordered internal structure of electrolyte membranes conducting lithium ions and their electrical conductivity (10-fold increase electrical conductivity in membranes subjected to the magnetic ordering). In both cases I was a leading author of the manuscripts and my contribution consisted of carrying out electrical (EIS) and X-ray (SAXS)

measurements and the analysis of collected data. In M13, I carried out in-situ measurements of electrical conductivity and SAXS studies of the membrane during magnetic ordering, identifying the critical stages of this process and the quantitative relationship between its internal structure and ion conductivity (M13). This subject has been further developed in my doctorate. In addition, I participated in studies of magnetic ordering of ultrafiltration membranes (D1) and colloidal systems composed of anisotropic nanoparticles (M8, M12, M14).

I have continued research of the magnetic alignment of polymeric materials in cooperation with prof. Osuji after obtaining the doctoral degree. This includes the recent publication D8 on the effects of magnetic alignment on electrical conductivity in lamellar BCPs. Publications D3 and D4 are the first reports in which the magnetic ordering of non-liquid crystalline block copolymers has been demonstrated. My contribution to this work consisted in using a novel method (described in the publication D2) developed with my cooperation to determine the average grain size in the studied block copolymer samples. This method, based on the analysis of the azimuthal distribution of Bragg reflexes in two-dimensional diffraction patterns is an alternative to the Scherrer's method of grain size determination based on analysis of the angular broadening of X-ray reflexes in powder diffractograms.

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## 7. OTHER SCIENTIFIC PUBLICATIONS AND ACHIEVEMENTS

### 7A. BIBLIOGRAPHIC SUMMARY OF PUBLICATION RECORD

Number of publications	31
Number of citations (average number of citations per item):	873 (28.2)
Number of publications after receiving PhD degree	16
Cumulative impact factor (according to the year published)	227.2
Hirsch index	20

(Data from Web of Science Core Collection Clarivate Analytics, entry date" 04.15.2019.)

### 7B. THE LIST OF PUBLICATIONS PUBLISHED AFTER RECEIVING THE PHD DEGREE NOT INCLUDED IN SERIES H1-H8

- D1. Gopinadhan, M.; Deshmukh, P.; Choo, Y.; Majewski, P. W.; Bakajin, O.; Elimelech, M.; Kasi, R. M.; Osuji, C. O. Thermally Switchable Aligned Nanopores by Magnetic-Field Directed Self-Assembly of Block Copolymers. *Adv. Mater.* 2014, 26 (30), 5148–5154. [17.493; 34]
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- D3. Rokhlenko, Y.; Gopinadhan, M.; Osuji, C. O.; Zhang, K.; O'Hern, C. S.; Larson, S. R.; Gopalan, P.; Majewski, P. W.; Yager, K. G. Magnetic Alignment of Block Copolymer Microdomains by Intrinsic Chain Anisotropy. *Phys. Rev. Lett.* 2015, 115 (25), 258302. [7,65; 25]
- D4. Rokhlenko, Y.; Majewski, P. W.; Larson, S. R.; Gopalan, P.; Yager, K. G.; Osuji C. O.; Implications of Grain Size Variation in Magnetic Field Alignment of Block Copolymer Blends. *ACS Macro Letters* 2017, 404-409. [6.131; 7]
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- D8. Majewski, P. W.; Gopinadham, M.; Osuji C. O. The effects of magnetic field alignment on lithium ion transport in a polymer electrolyte membrane with lamellar morphology, *Polymers*, 2019 accepted

## 7C. THE LIST OF PUBLICATIONS PUBLISHED BEFORE RECEIVING THE PHD DEGREE

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- M3.** Majewski, P. W.; Osuji, C. O. Non-Degenerate Magnetic Alignment of Self-Assembled Mesophases. *Soft Matter* 2009, 5 (18), 3417–3421. [4,869; 17]
- M4.** Gopinadhan, M.; Majewski, P. W.; Osuji, C. O. Facile Alignment of Amorphous Poly(ethylene Oxide) Microdomains in a Liquid Crystalline Block Copolymer Using Magnetic Fields: Toward Ordered Electrolyte Membranes. *Macromolecules* 2010, 43, 3286–3293. [4,837; 57]
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