Block Copolymer Thin Films: Characterizing Nanostructure Evolution with *In Situ* X-Ray and Neutron Scattering

Cameron K. Shelton^a and Thomas H. Epps, III^{a,b,*}

^aDepartment of Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States

^bDepartment of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, United States

*Address correspondence to thepps@udel.edu

KEYWORDS: block copolymer thin film, annealing, nanostructure reorganization, *in situ* characterization, X-ray scattering, neutron scattering

ABSTRACT

Block copolymer (BCP) thin films have attracted significant attention as lithographic templates, separation membranes, and organic photovoltaic active layers for emerging nanotechnologies due to their ability to self-assemble into nanoscale features. To direct the self-assembly of BCP thin film nanostructures into ordered arrays, a suite of annealing techniques have been developed (*e.g.* thermal annealing, solvent vapor annealing, magnetic/electrical field alignment), each with its own set of controllable parameters and mechanisms for nanostructure reorganization. In this Review, we discuss the importance of *in situ* X-ray and neutron scattering for the study of BCP thin films subjected to different annealing protocols. These scattering approaches have become vital for understanding the complex nanostructure reorganization processes inherent in thin film fabrication and for establishing more consistent control over the morphology, ordering, and orientation. A major advantage of *in situ* X-ray and neutron scattering characterization is the ability to link the thermodynamic and kinetic pathways of nanostructure evolution over macroscopic (several cm^2) areas during annealing or processing. This feature has made *in situ* X-ray and neutron scattering ideal for refining annealing techniques, fostering robust assembly protocols, and developing the next-generation of directed assemblies. As the toolbox of viable processing methods continues to grow, we highlight

potential opportunities to enhance current X-ray and neutron scattering capabilities through the improvement of scattering facilities, techniques, sample chambers, scattering/annealing protocols, and model development to establish universal control over BCP thin film self-assembly.

1. Introduction

With their ability to self-assemble into periodic arrays of nanoscale features, block copolymer (BCP) thin films have garnered significant interest for use in nanolithographic, photovoltaic, and separation membrane applications that require ordered structures at length scales that are not easily achieved with traditional photolithography techniques (< 30 nm) [1-7]. In BCP thin films, the interplay between bulk (Flory-Huggins interaction parameter[s], degree of polymerization, and block volume fractions) and confinement (film thickness and substrate/free surface interactions) effects governs the resulting nanostructured assembly, altering the morphology, orientation (features parallel or perpendicular to the substrate), and ordering [8-13]. Additionally, thin film deposition methods (*e.g.*, spin-casting, flow coating, dip coating, zone-casting, electrospray) can greatly affect the as-cast morphology [10,14-17]. To guide phase separation for a given application, BCP thin films often are subjected to various post-processing techniques designed to modulate specific interactions [9-11,18]. Common avenues include thermal annealing [19,20], solvent vapor annealing (SVA) [21-23], solvothermal annealing [24-26], microwave-assisted SVA [27,28], chemical substrate modification and patterning [29-33], graphoepitaxy [34-37], electrical/magnetic field alignment [38-42], and shear alignment [43-49], each of which has its own set of advantages and disadvantages [3,11,18,50,51]. All of these techniques have been restricted in widespread industrial applications due to several challenges, including fine-tuning of the key, system-dependent parameters that direct self-assembly, limited universality over a growing number of BCP systems/architectures, and a propensity for high defect densities. To address these challenges, it is imperative to understand the inherent mechanisms behind each annealing technique to achieve cost-effective and scalable control over the morphological evolution [52]. Specifically, the development of characterization tools that

identify and link the kinetic and thermodynamic pathways for domain reorganization are required to optimize annealing conditions and advance thin film processing techniques that foster universal control over BCP thin film self-assembly.

In situ characterization techniques offer an innovative perspective on self-assembly mechanisms by tracking temporal restructuring as influenced by particular processing techniques or sample environments (*e.g.* variable temperature, solvent atmosphere, electromagnetic field). Additionally, the use of *in situ* characterization tools can help identify the underlying driving forces for nanostructure evolution, such as intermediate pathways to domain restructuring from as-cast to annealed states [42,53-55]. Due to these advantages, *in situ* characterization of BCP thin films has provided key fundamental insights into various annealing approaches. For example, optical microscopy (OM) during thermal annealing has been employed to probe the kinetics of micron-scale surface structure development and growth (*e.g.* island/hole formations), which can be related to substrate/free surface and film thickness effects on nanoscale self-assembly [32,56,57]. Additionally, *in situ* atomic force microscopy (AFM) has been used to examine nanoscale restructuring during thermal annealing [58-65], electrical field alignment [66], and SVA [67-71]. As a further example, researchers have conducted spectral ellipsometry (SE) and reflectometry (SR) experiments during SVA to measure film thickness (*i.e.* polymer/solvent volume fraction) changes during swelling and deswelling [72-78]. Data from these SE/SR measurements have been analyzed to calculate polymer-solvent interaction parameters [67,79], construct surface structure phase diagrams [23,80], and understand thickness dependent self-assembly mechanisms [39,77,81,82]. Researchers also have followed changes in nanoscale phase separation with transmission electron microscopy (TEM) during nanoindentation, or infrared Raman spectroscopy (IR-RS) during thermal annealing [83,84].

Unfortunately, each technique can be limited by factors such as small-area or two-dimensional data collection (AFM, TEM), inability to image nanoscale features (OM, SE/SR, IR-RS), sample preparation difficulties (TEM), and lack of through-film characterization (AFM).

As complements to *in situ* microscopy and spectral characterization, *in situ* X-ray and neutron scattering are powerful techniques that provide nanoscale, large-area, high-resolution, and through-film information about BCP domain restructuring [11,50,51,85-89]. The respective wavelengths of X-ray and neutron radiation are ideally suited to study the pertinent size scales of BCP self-assembly (nm to μm) over macroscopic areas (up to several cm^2), allowing less-invasive analysis and improved statistics (large interrogation areas) in comparison to other characterization techniques (see Figure 1) [86,90,91]. X-rays and neutrons also are highly penetrating, permitting through-film structural analysis of in-plane (transmission geometry) and out-of-plane (reflection geometry) features. However, *in situ* analyses of BCP thin films with X-ray and neutron scattering requires engineered sample chambers, refined experimental protocols, and sophisticated data analysis tools in order to create sample annealing environments (*e.g.* temperature cells, shear cells, humidity chambers), maximize resolution, and minimize data collection times for kinetic analysis. Herein, we review state-of-art *in situ* X-ray and neutron scattering techniques to investigate BCP self-assembly in thin films subjected to various annealing conditions. Additionally, we highlight the advantages of X-ray and neutron scattering, directly relate the insights gained from *in situ* studies to the advancement of BCP thin film processing conditions and techniques, and present several future opportunities for scattering development.

Figure 1: Common characterization techniques used to analyze BCP thin film self-assembly. Many techniques, such as AFM, TEM, and SEM, only probe nanoscale areas and features, and others, such as OM, only probe microscale areas and features. X-ray and neutron scattering techniques allow interrogation of nanoscale and microscale features over macroscopic areas, which provides statistically significant (*i.e.*, large area) and more universal results.

This review is organized as follows. First, *in situ* X-ray characterization techniques including small- and wide-angle X-ray scattering (SAXS and WAXS, respectively), X-ray reflectivity (XRR), and grazing-incidence small-angle X-ray scattering (GISAXS) will be discussed. Additionally, several promising X-ray scattering techniques, such as those incorporating low-

energy X-ray scattering (*e.g.*, resonant soft X-ray scattering [RSoXS]), will be described. Next, *in situ* neutron scattering methods such as small-angle neutron scattering (SANS) and rotational SANS (RSANS), neutron reflectivity (NR), and grazing-incidence small-angle neutron scattering (GISANS) will be detailed. Finally, this review will summarize key challenges associated with *in situ* X-ray and neutron scattering techniques and highlight potential opportunities for *in situ* X-ray and neutron methods that will enhance understanding of self-assembly in BCP thin films.

2. X-ray Scattering

In situ X-ray scattering has been used to probe the evolution of in- and out-of-plane features in a wide variety of BCP thin film systems [51,92,93]. X-rays interact with the electron clouds of individual atoms and scatter depending on the composition of the sample; X-rays scatter off atoms with large atomic masses (*e.g.*, ruthenium, osmium) more strongly than atoms with small atomic masses (*e.g.*, hydrogen) [94]. Although, X-rays can scatter either elastically (no momentum transfer; *e.g.*, SAXS, WAXS, GISAXS) or inelastically (momentum transfer; *e.g.*, X-ray Raman spectroscopy, Compton scattering, resonant inelastic X-ray scattering), the discussion herein is restricted to elastic scattering [94]. For a detailed explanation of X-ray scattering, the reader is directed to the literature [86,95,96]. Key advantages of X-ray scattering for *in situ* experiments are high flux, low divergence, and limited wavelength spread; the combination of these factors enhances X-ray use in studies that require fast data collection times and high resolution. Additionally, a moderate X-rays flux can be achieved in laboratory-scale instruments, making X-ray scattering more accessible than neutron scattering for exploratory studies on BCP thin films.

2.1 Transmission X-ray scattering for in-plane analysis of thin films

SAXS and WAXS operate in transmission geometries to measure scattering from in-plane features at different scattering angles (*i.e.*, different length scales); SAXS typically measures scattering from a q range of approximately $10^{-3} \text{ \AA}^{-1}$ to $10^0 \text{ \AA}^{-1}$ (μm to nm size scale analysis) and WAXS typically measures scattering from a q of approximately $10^{-2} \text{ \AA}^{-1}$ to $10^1 \text{ \AA}^{-1}$ (nm to $\text{\AA}$ size scale analysis) [97-99]. Using *in situ* SAXS and WAXS during thermal annealing, BCP domain rearrangement has been studied on chemically-patterned substrates [100,101], during SVA [102], during electric field exposure [103,104], and upon drying after film casting [54,105-108]. For example, Gu *et al.* employed SAXS during thermal annealing to examine the complex restructuring behavior of polystyrene/polylactide brush BCP films (see Figure 2) [109]. Their efforts suggested that the time-scales for nanostructure reorganization were significantly reduced for brush BCPs (≈ 30 min) in comparison to their linear analogs (>24 h) as a result of the reduction in polymer chain entanglements. In other work, Thurn-Albrecht *et al.* demonstrated how *in situ* SAXS could follow the electrical field alignment of poly(styrene-*b*-methyl methacrylate) (PS-PMMA) domains through an order-to-disorder transition (ODT) [42]. From this study, the dominant alignment mechanism was identified as the breakup and reformation of ordered grains rather than the reorientation of large grains. Studies such as these are useful in the design of well-aligned nanomaterials with low defect densities. Similarly, by using *in situ* SAXS to track the kinetics of domain rearrangement in poly(styrene-*b*-isoprene) (PS-PI) and poly(styrene-*b*-isoprene-*b*-styrene) (PS-PI-PS) thin films in an electrical field (see Figure 3) [110], DeRouchey *et al.* found that an intermediate, partially disordered state promoted the breakup of large ordered grains and facilitated reorientation. In general, *in situ* SAXS and

WAXS studies offer a relatively straightforward approach for the examination of in-plane domain reorganization during various annealing processes in BCP thin films.

Figure 2: Schematic of lamellar-forming polystyrene/polylactide brush BCP (top) and resulting *in situ* SAXS patterns (peaks labeled with arrows) during thermal annealing at 130 °C (bottom). Each set of SAXS patterns indicates a different molecular weight of the backbone at the same graft molecular weight of polystyrene ($[\text{g-S}_{2.4\text{k}}]$) and polylactide ($[\text{g-LA}_{2.4\text{k}}]$): (a) $[\text{g-S}_{2.4\text{k}}]_{35}\text{-}b\text{-}[\text{g-LA}_{2.4\text{k}}]_{43}$, (b) $[\text{g-S}_{2.4\text{k}}]_{51}\text{-}b\text{-}[\text{g-LA}_{2.4\text{k}}]_{67}$, and (c) $[\text{g-S}_{2.4\text{k}}]_{98}\text{-}b\text{-}[\text{g-LA}_{2.4\text{k}}]_{124}$. *In situ* SAXS indicated that the time scales for nanostructure reorganization increased with the molecular weight of the brush's backbone but were significantly reduced in comparison to linear analogs of the same molecular weight. Adapted with permission from ref [109]. Copyright 2013 American Chemical Society.

Figure 3: Plot of the q dependence of the scattering intensity for the intermediate and final state of orientation on PS-PI during electrical field alignment. The broadening of the intensity peak and the shift to higher q noted at the intermediate state indicates partial disordering of the microphase structure. Adapted with permission from ref [110]. Copyright 2004 American Chemical Society.

Notably, SAXS and WAXS examinations of BCP thin films are limited by the relatively small scattering volumes, the potential for radiation damage to the film, and inadvertent structural reorganization from sample interactions with X-rays [111-113]. As an alternative to SAXS and WAXS, RSoXS reduces film damage and unintentional domain restructuring through the use of low-energy radiation [112]. Additionally, RSoXS is more capable of discerning the chemical dissimilarities between organic components by providing increased contrast and resolution in comparison to SAXS [113]. For example, researchers have exploited RSoXS capabilities to distinguish between multiple domains in triblock polymer films [114] and to analyze nanostructured films as thin as one monolayer (≈ 50 nm) [113], experiments that would be extremely difficult with conventional SAXS [115]. Although several investigations of BCP thin

films with RSoXS are found in the literature [112-114,116,117], reports of *in situ* RSoXS studies of BCP film domain reorganization are not as notable, likely because grazing-incidence geometries, which measure in-plane and out-of-plane features simultaneously, have to date been more informative scattering techniques for the study of BCP thin films [118].

2.2 GISAXS for in-plane and out-of-plane characterization

As opposed to the transmission geometries of SAXS, WAXS, and RSoXS, reflectivity geometries typically are used to study the through-film structural changes during exposure to different stimuli. GISAXS and XRR techniques can be applied in this context; however, *in situ* XRR experiments on BCP thin film processing are not prevalent in the literature. The comparative lack of *in situ* XRR studies likely is because XRR only characterizes out-of-plane features of the film, while GISAXS can probe in-plane and out-of-plane features simultaneously [119-123]. The combination of transmission (in-plane features) and reflectivity (out-of-plane features) profiles with high resolution at reasonable time scales (seconds to minutes time resolution; high X-rays flux) makes GISAXS ideal for *in situ* studies of BCP thin films. Through *in situ* GISAXS studies, researchers have examined key self-assembly phenomena including thermal/phase transitions (*e.g.* ODTs, order-order transitions [OOTs], T_g 's, T_m 's) [124-133], water/solvent uptake [73,134-144], and domain restructuring [19,100,145-149]. For example, Shin *et al.* examined differences in the microphase OOT behavior (lamellae [LAM] → hexagonally-perforated lamellae [HPL] → gyroid [GYR] → hexagonally-packed cylinders [HEX] → disordered [DIS]) in bulk and thin film PS-PI BCPs with GISAXS during thermal annealing [127]. They attributed differences in the OOT temperatures, as well as the disappearance of a HEX transition between the GYR and DIS phases in the thin film samples, to

substrate and free surface interactions that skewed the self-assembly behavior (see Figure 4). The real-time, high-area analysis capabilities of GISAXS offered a facile and more statistically significant means to identify the precise OOT temperatures and morphologies.

Figure 4: Maximum peak intensities at scattering angles related to the (102) and $(2\bar{1}1)(1\bar{1}2)$ planes. The OOT temperatures (vertical dotted blue lines) in thin film geometries were determined by the significant changes in scattering intensities from the highlighted planes and confirmed by analyzing the full GISAXS patterns. Above the plot, transition temperature windows in thin film geometries are compared with those in bulk. Adapted with permission from [127]. Copyright 2009 American Chemical Society.

Complex BCP thin film systems such as salt-doped films, films with more than two chemically-distinct domains (*e.g.*, ABC triblock terpolymers), and thermally responsive films also have been explored with *in situ* GISAXS [148,150-152]. For example, Rho *et al.* investigated the self-assembly of a nine-arm star PS_3 -(poly[4-methoxystyrene])₃-PI₃ (PS_3 -PMOS₃-PI₃) BCP thin film [148]. In their work, star BCP thin films were monitored during

thermal annealing to reveal intricate restructuring mechanisms during heating and cooling cycles, including the presence of rotational isomers of a HEX and triangular prism morphology that formed during cooling (see Figure 5) [148]. As the number of BCP chemistries, architectures, and morphologies grows exponentially [52], results from *in situ* GISAXS studies, such as those described above, are instrumental in the design of annealing protocols that reduce structural defects and control the through-film uniformity of various nanostructures.

Figure 5: (a) An in-plane oriented HEX truncated PS cylinder and PMOS triangular prism separated nanostructure (Type-A HEX) in a $\text{PS}_3\text{-PMOS}_3\text{-PI}_3$ star polymer film after SVA with chloroform. The Type-A HEX morphology persisted when the film was subsequently heated from 25 °C to 190 °C. (b) A mixture of the Type-A HEX structure and its rotational isomer (Type-B HEX) formed when the film was heated to a temperature between 190 °C and 220 °C following SVA. (c) A mixture of the Type-A and Type-B HEX structures remained in the film upon cooling from 220 °C to 30 °C. Adapted with permission from ref [148]. Copyright 2013 American Chemical Society.

Recently, *in situ* GISAXS during SVA has been used to investigate how factors such as solvent choice [153,154], solvent partial pressure [55,133,139,153,155], swelling/deswelling rates [55,156,157], and film thickness [141,155] affect the restructuring of BCP thin film domains. This ability to track nanostructure evolution from as-cast, to swollen, to deswollen states during SVA has provided some of the most compelling information on domain restructuring phenomena to date [51]. For example, Chavis *et al.* used solvent mixtures of tetrahydrofuran (THF) and methanol (MeOH) to anneal poly(2-hydroxyethyl methacrylate-*b*-methyl methacrylate) (PHEMA-PMMA) thin films [153]. By modulating the composition of the (SVA) solvent mixture and simultaneously monitoring the change in morphology from as-cast to organized lamellae and cylinders, the researchers quantified solvent mixture compositions associated with each change in morphology and linked solvent-swollen polymer volume fractions to PHEMA-PMMA phase diagrams (see Figure 6). Additionally, by manipulating several key annealing parameters including degree of swelling, annealing time, solvent preference, and quench rate, Chavis *et al.* formed metastable gyroid and sphere morphologies in their thin films [153]. In similar work, Paik *et al.* employed solvent mixtures of acetone and THF to study the reversible microphase transition between spheres and cylinders in poly(α -methylstyrene-*b*-4-hydroxystyrene) thin films [154]. Using *in situ* GISAXS, they related changes in polymer domain volume fractions, degrees of domain plasticization, and subsequent trapping of morphologies in quenched films to specific thermodynamic and commensurability effects that directed nanostructure reorganization.

Figure 6: AFM and GISAXS results for PHEMA-PMMA films from different solvent annealing treatments and after subsequent film drying. a,b) As-cast, no anneal; c,d) parallel lamellae, annealed for 45 min in 80/20 vol/vol THF/MeOH; e,f) gyroid, annealed for 45 min in 50/50 vol/vol THF/MeOH g,h) parallel cylinders, annealed for 45 min in 20/80 vol/vol THF/MeOH; i,j) sphere, annealed for 3-4 h in 50/50 vol/vol THF/MeOH. Adapted with permission from ref [153]. Copyright 2015 John Wiley & Sons, Inc.

Kinetic studies of BCP thin film domain restructuring during SVA also have been conducted *via* GISAXS [135,136,140]. Through these studies, researchers have developed morphology-related design rules for specific polymer/solvent systems [153,154], investigated changes to layer ordering and thickness during deswelling [55,156], and tracked kinetic pathways for orientation changes during solvent exposure [158]. For example, Zhang *et al.* monitored the swelling and deswelling of poly(styrene-*b*-butadiene) (PS-PB) thin films subjected to ethyl acetate vapor [136]. They obtained detailed information on the change in lamellar domain spacing at different

swollen film thicknesses (measured by polymer volume fraction). Their studies, on both parallel- and perpendicular-oriented lamellar nanostructures, uncovered the presence of three swelling (solvent uptake) and two drying (deswelling) kinetic regimes; each regime was attributed to the particular chain dynamics at a given solvent swollen state and provided an improved mechanistic understanding of SVA swelling and deswelling.

The simultaneous collection of in-plane and out-of-plane structural information has made grazing-incidence scattering geometries highly attractive for BCP thin film analysis. As a result, several modifications to GISAXS have been developed to probe the finer details of nanomaterials processing. One recent example is microbeam GISAXS (μ GISAXS) that can measure local structural information over a significantly smaller area (several μm^2 or less) in comparison to GISAXS (several cm^2) [159,160]. For instance, Abul Kashem *et al.* used μ GISAXS to examine the local deposition of iron in etched BCP thin film templates [161]. Three distinct nanostructure growth regions were detected, which suggested that the deposited iron preferentially wet the copolymer pores as opposed to the top surface of the template (nanostructure iron height $[H] > \text{nominal iron height } [h_n]$) until a critical height was reached ($H \approx 4 \text{ nm}$) (see Figure 7). Results such as these can be used to design more efficient deposition methods to evenly-coat nanotemplated features for numerous applications [6,10,162-166]. Although, other characterization methods, such as AFM and TEM, can provide localized details *ex situ*, μ GISAXS provides localized mapping of both 2D and 3D morphologies, making this deposition study possible.

Figure 7: (a) Intensities from the off-detector cuts of *in situ* μ GISAXS data (symbols) and the corresponding fits from simulations (solid lines). Data are plotted as a function of $\varphi = \alpha_i + \alpha_f$, in which α_i is the incident angle of the X-ray beam on the sample, and α_f is the exit angle of the scattered beam. The curves are shifted vertically for visual clarity. The nominal heights of the sputter-deposited iron are shown to the right of the corresponding curves. (b) Extracted object heights (H) of the nanostructures plotted as a function of nominal height (h_n). A, B, and C indicate the three regimes of nanostructure growth with linear fits (solid lines). (c) Schematic side view of the basic setup used in the *in situ* μ GISAXS experiments during sputter deposition. Adapted with permission from ref [161]. Copyright 2011 American Chemical Society.

Other recent offshoots of GISAXS include nanobeam GISAXS (*n*GISAXS), grazing-incidence RSoXS (GI-RSoXS), and critical-dimension SAXS (CDSAXS) [121, 167]. With *n*GISAXS, the

X-ray beam size is decreased further (as small as 300 nm diameter) to probe the through-film profile across localized areas [121]. To improve contrast between domains, GI-RSoXS incorporates low-energy, or “soft” X-rays to measure depth-resolved structure and composition profiles [168,169]. Additionally, as an alternative to traditional GISAXS, CDSAXS examines buried interfaces by collecting 2D profiles from multiple transmission scattering angles to construct a 3D reciprocal-space map of periodic nanostructures [170-172]. This approach eliminates difficult modeling from a single, complex GISAXS pattern. Finally, resonant, low-energy radiation can be combined with CDSAXS (res-CDSAXS) to provide resonant scattering contrast between BCP components [173]. Although *in situ* studies of BCP thin films with *n*GISAXS, GI-RSoXS, and res-CDSAXS are not highlighted currently in the literature, these techniques offer promising solutions for analyzing the transient behavior in BCP thin films of increasing complexity.

2.3 Sample chambers for *in situ* X-ray scattering analysis

To study a wider variety of annealing environments and conditions with *in situ* X-ray scattering, specially-designed chambers have been developed. For example, sample chambers with precise temperature control have facilitated *in situ* investigations of thermal annealing processes [160,174], while sample chambers with controlled solvent atmospheres and inline monitoring have been built to permit *in situ* SVA studies (see Figure 8a) [139,153,155]. Similar sample chambers and configurations have been constructed to probe the effects of electrical/magnetic fields [103,175], solvent drying from the film after SVA or casting [105,106], and UV exposure [176]. For example, Stegelmeier *et al.* built a custom blade-casting apparatus to track the structural evolution of domains immediately after film casting *via* SAXS (see Figure

8b) [106]. Their results elucidated key parameters that influence nanostructure self-assembly before annealing. As discussed previously with μ GISAXS, innovative *in situ* chambers have been built to study the deposition of materials within BCP thin film templates [161,177-182]. As two additional examples, flow-deposition (see Figure 8c) and sputter-deposition (see Figure 8d) chambers enable the investigation of nanowire and nanocluster growth in BCP thin film templates. Results from these studies are used to identify kinetic pathways and develop precise control over templated nanostructure deposition [161,177,179]. The design and fabrication of *in situ* chambers continues to be an important aspect in the investigation of BCP thin films, allowing researchers to further probe the nanostructure self-assembly during exposure to various processing environments. Several future opportunities for *in situ* chamber design are highlighted in Section 4.2.

Figure 8: Illustrations of *in situ* X-ray scattering sample chambers used to study (a) the evolution of nanostructured poly(α -methylstyrene-*b*-4-hydroxystyrene) films during SVA [154], (b) the evolution of nanostructures in a poly(styrene-*b*-4-vinylpyridine) film after blade-casting [106], (c) the deposition and growth of gold in poly(styrene-*b*-ethylene oxide) channels *via* a flow stream method [178], and (d) the sputter deposition of gold in poly(styrene-*b*-isoprene) film templates [179]. Adapted with permission from refs [154] (Copyright 2010 American Chemical Society), [106] (Copyright 2015 American Chemical Society), [178] (Copyright 2009 American Chemical Society), and [179] (Copyright 2008 American Chemical Society).

3. Neutron Scattering

In comparison to X-rays, neutrons have no charge and no electric dipole moment [90]. Therefore, neutrons travel unperturbed through electron clouds and instead are affected by interactions with nuclei (*i.e.*, nuclear scattering), resulting in a greater penetration depth and less beam-induced damage in comparison to X-rays [94]. Additionally, although neutron sources cannot produce the same flux as X-ray sources (10^{14} neutrons/s *vs.* 10^{18} photons/s), neutron scattering has three key advantages for the study of BCP thin films: (1) neutrons can distinguish smaller atoms (*e.g.* hydrogen) even in the presence of larger atoms; (2) the scattering cross section of similarly sized atoms can vary greatly and generate natural contrast between polymer domains with relatively similar chemical components; and (3) the scattering of neutrons can be selectively altered through isotopic replacement [85,87,90]. This isotopic replacement is arguably the most important feature for polymer studies and is referred to as contrast variation or contrast matching [183]. By selectively manipulating the isotopic makeup of different polymer blocks, commonly by replacing hydrogen with deuterium, neutron scattering can provide highly-resolved information about individual domains of self-assembled BCPs [184-186]. For a more detailed explanation of neutron scattering theory and its advantages for BCP systems, the reader is directed to several sources [87,88,183,187,188]. Overall, the features of neutron scattering make the technique an indispensable tool to probe the behavior of nanostructured systems [189].

Although neutron scattering is potentially ideal for BCP thin film studies, neutrons for scattering experiments are produced by either nuclear fission (continuous source) or spallation (pulsed source), and both methods are highly expensive (approximately \$1.5 billion to construct sources and \$140 million per year to operate [190], in comparison to a range of \$150 million to \$800 million to construct synchrotron sources) [191,192]. Furthermore, neutron scattering is

unfeasible for most laboratory-scale setups, in contrast to X-ray scattering. Currently, there are over thirty neutron scattering facilities in operation around the world, including the High Flux Isotope Reactor (HFIR), the highest flux reactor-based neutron source in the United States, at Oak Ridge National Laboratory [193,194]. Planned facilities include the advanced European Spallation Source (ESS), which will use state-of-the-art spallation technology to improve upon the neutron fluxes available from continuous sources [183,195].

3.1 SANS for in-plane structure analysis

SANS uses a transmission geometry to measure in-plane structural and compositional changes in nanostructured thin films [189,196-198]. To overcome the difficulty of low flux and small sample volumes for transmission geometries, contrast variation provides a means to increase the scattering between individual domains and obtain more meaningful (*i.e.*, statistically significant) scattering profiles. For example, Xu *et al.* conducted SANS while applying an electrical field to demonstrate how the alignment of lamellar-forming *d*PS-PMMA (deuterated PS and non-deuterated PMMA) thin films improved due to the reduction in substrate and free surface effects in cases for which the film thickness was greater than $10 L_0$ [38]. In this instance, the PS block was deuterated to increase the scattering length density (ρ) between polymer domains from $\Delta\rho_{PS/PMMA} = 0.3 \times 10^{-6} \text{ \AA}^{-2}$ to $\Delta\rho_{d-PS/PMMA} = 5.3 \times 10^{-6} \text{ \AA}^{-2}$ at 25 °C. For comparison, a similar change in $\Delta\rho$ between non-deuterated and deuterated PS-PI-PS films ($\Delta\rho_{PS-PI-PS} = 1.1 \times 10^{-6} \text{ \AA}^{-2}$ to $\Delta\rho_{dPS-PI-dPS} = 6.2 \times 10^{-6} \text{ \AA}^{-2}$ at 25 °C) [199] led to a significant decrease in scattering time from hours to minutes [200].

As an alternative to contrast variation, scattering intensity also has been improved through the use of thicker or stacked films to increase sample volume [53,201,202]. For example, Park and

Balsara used SANS during thermal annealing and relatively thick films (50-180 μm) to track the ODT of poly(styrenesulfonate-*b*-methylbutylene) (PSS-PMB) BCPs with varying degrees of sulfonation [201]. The measured ODT temperatures were used to calculate polymer-polymer Flory Huggins interaction parameters, and ultimately predict domain spacings/morphologies, as a function of sulfonation extent. This analysis provided insight into the effect of segregation strength on restructuring pathways during thermal annealing and helped design annealing protocols to stabilize complex morphologies (*e.g.*, gyroid).

The combination of increasing film thickness and incorporating contrast variation to improve resolution and decrease measurement time-scales also has been demonstrated. Kim *et al.* paired thick films (110-170 μm) with deuterated water (D_2O) and SANS during SVA experiments to study the effect of temperature on the water uptake and morphology of PSS-PMB [202]. The higher ρ of D_2O ($6.4 \times 10^{-6} \text{ \AA}^{-2}$) in comparison to fully sulfonated PSS ($2.1 \times 10^{-6} \text{ \AA}^{-2}$) at 25 $^\circ\text{C}$ was used to quantify the D_2O concentration within individual domains, while the thick films provided statistically significant scattering intensities over a large q range ($0.03 \text{ \AA}^{-1}$ to $0.6 \text{ \AA}^{-1}$). Thus, the authors were able to detect significant D_2O contents in the nominally hydrophobic PSS domains, which likely were responsible for the rapid proton transfer seen in low molecular weight PSS-PMB BCPs (see Figure 9) [203]. These SANS experiments demonstrate how neutron scattering allows researchers to relate kinetic pathways for restructuring to thermodynamic driving forces, while also detecting compositional changes in nanostructured films. However, even with contrast variation, the sample volume constraints limit the effective use of *in situ* SANS in kinetic studies of ultrathin ($< 100 \text{ nm}$ thick) films with current neutron flux limitations (see Section 4.1).

Figure 9: *In situ* SANS profiles with highlighted Bragg peaks (inverted open triangles; hexagonal cylinder morphology) for 19 mol% sulfonated PSS-PMB exposed to D₂O/air environment at different relative humidities (RH) and temperatures. To obtain the SANS profiles, two different sample-to-detector distances (12 m and 1 m) were used as represented by darker ($q < \approx 0.4 \text{ nm}^{-1}$) and lighter curves ($q > \approx 0.4 \text{ nm}^{-1}$), respectively. When the temperature was increased at fixed RH = 95%, the formation of a water domain was noted (black arrow). Inset plot displays the degree of hydration (λ) as a function of temperature at RH = 95%. Adapted with permission from ref [202]. Copyright 2010 American Chemical Society.

3.2 NR for out-of-plane structure analysis

As a complement to SANS, NR employs a reflection geometry to probe out-of-plane structures (specular reflection) [85,186]. Because the path length of the neutrons through the sample is longer in reflection geometries, some of the sample volume issues associated with SANS are mitigated in NR. Furthermore, the same SANS contrast variation techniques can be applied to NR. For example, Foster *et al.* used deuterium labeling of a lamellar-forming poly(ethylene–propylene-*b*-ethylethylene) (PEP-PEE) BCP thin film combined with NR during thermal annealing to explore ODTs, changes in substrate/free surface wetting behavior, through-film nanostructure ordering, and the characteristic dimension of BCP films as a function of temperature [204]. Two different deuterated compositions (non-deuterated PEP with deuterated PEE and deuterated PEP with deuterated PEE) were used to provide several levels of contrast for analysis. By measuring the substrate-to-free surface compositional profile at elevated temperatures, the researchers identified three distinct lamellar regimes that corresponded to a transition from the strong to intermediate to weak segregation.

Traditionally, *in situ* NR analysis has been employed to measure through-film solvent concentration profiles (*e.g.* water and organics) in BCP thin films by controlling solvent-polymer and polymer-polymer contrast with selective deuteration. Achieving similar contrast with other characterization techniques is extremely difficult. For example, using deuterated water (D₂O) and a non-deuterated BCP, Zhong *et al.* measured the through-film concentration of D₂O in lamellar domains of a thermoresponsive poly(styrene-*b*-methoxydiethylene glycol acrylate-*b*-styrene) (PS-PMDEGA-PS) film during hydration, drying, and rehydration cycles [205,206]. NR profiles indicated that D₂O motion was hindered by periodic PS domains and that a D₂O wetting layer formed at the free surface (see Figure 10). Additionally, they noted that the critical

edge and overall scattering intensity increased with time, which suggested D₂O was diffusing into the film. However, this diffusion did not result in an overall film thickness change, which provided key insights regarding the unique swelling behavior of the hydrogel PMDEGA layers. Understanding this type of intricate process is key in the development of thermoresponsive polymer films for specific applications such as sensors, actuators, coatings, and switches [205].

Figure 10: (a, top) NR curve of a semi-swollen PS-PMDEGA-PS film 30 s after the temperature was decreased from 35 °C to 23 °C (black dots), shown together with a model fit (red line). (a, bottom) Resulting ρ (SLD) profile from NR curve. Position $Z = 0$ on the x-axis represents the top surface of the silicon oxide layer at the substrate surface. (b, top) Volume fraction of D_2O ($\phi_{\text{D}_2\text{O}}$) in the top (black open circle) and middle (red open circle) PS layers as a function of time. (b, bottom) Volume fraction of D_2O in the top (black, filled circles) and bottom (red, filled circles) PMDEGA layers as a function of time when the temperature was decreased from 45 °C to 23 °C. The change in $\phi_{\text{D}_2\text{O}}$ in the two PMDEGA layers indicates the PS limits D_2O diffusion through the film, preventing full hydration of the bottom PMDEGA layer. Adapted with permission from ref [205]. Copyright 2015 American Chemical Society.

Simultaneous tracking of water/solvent concentration and resulting nanostructure changes also can be achieved with *in situ* NR and selective deuteration as demonstrated by Torikai and coworkers [126]. The authors investigated the temporal response of poly(styrene-*b*-2-vinylpyridine) thin films exposed to D₂O and deuterated toluene (*d*-toluene). Interestingly, D₂O, which is considered a non-solvent for both blocks, penetrated the film and caused structural changes, while *d*-toluene (good solvent) exposure resulted in complete dissolution of the film. In a similar hydration study, Kamata *et al.* examined the swelling kinetics and structural changes of a poly(ethylene oxide-*b*-butylene oxide) (PEO-PBO) thin films immersed in D₂O [134]. They measured rapid swelling behavior and distinct swelling regimes that significantly impacted the ordering and orientation of the PEO-PBO films with statistically significant scattering profiles captured every 10 min. Insights gained from these studies, and the development of similar experiments, could be used to create faster, highly efficient, and more universal SVA methods such as direct immersion annealing [207].

As separate techniques, SANS (in-plane) and NR (out-of-plane) each provide only a single piece of the structural information ideal for BCP thin film studies. To generate a more complete picture of BCP thin film domain reorganization, *in situ* SANS and NR measurements recorded under the same experimental conditions enables multidimensional analysis. Shelton *et al.* used this approach to examine the effect of solvent-polymer interactions on the self-assembly of a cylinder-forming PS-PI-PS film exposed to deuterated benzene vapor [33]. SANS was conducted to identify the distribution of solvent into individual domains and the changes in domain spacing as a function of solvent partial pressure. Meanwhile, NR was used to track the substrate to free surface distribution of solvent and measure the change in film thickness, vertical layer spacing, and the number of stacked layers as a function of solvent partial pressure. The

combined results indicated two regimes of out-of-plane nanostructure reorganization (either changing layer thickness at constant number of layers or changing number of layers at constant layer thickness), and the transition between each regime was directly related to the plasticization of the glassy PS block. With *in situ* neutron scattering, a better understanding of solvent effects on individual domains of a BCP thin film can be used to facilitate the design of solvent conditions necessary for the desired morphology and through-film periodicity.

3.3 Advanced neutron scattering configurations for multidimensional analysis

As an alternative to separate SANS and NR experiments, off-specular (or diffuse) NR, grazing-incidence small-angle neutron scattering (GISANS), and rotational small-angle neutron scattering (RSANS) are being developed to study in-plane and out-of-plane features of BCP thin films simultaneously [121,123,183,208]. For example, Wang *et al.* employed specular and off-specular neutron reflectivity to explore the distribution profile of D₂O in poly(styrene-*b*-*N*-isopropylacrylamide) thin films [209,210]. This combination of techniques helped identify the mechanism by which the films absorbed large amounts of water (≈ 17 vol% water) without significant swelling. However, multidimensional studies are not prevalent in BCP thin film literature, likely due to the large measurement time-scales, on the order of several hours, and limited modeling protocols [211].

A newly developed neutron scattering technique, RSANS offers a unique approach to obtaining through-film structural information. By rotating the sample in the neutron beam, RSANS provides a full 3D profile from a series of 2D scattering patterns (see Figure 11) [212]. Using RSANS, researchers have probed the effect of substrate roughness on BCP thin film nanostructure orientation [213-215], identified thickness effects on through-film structural

uniformity [216], and characterized domain reorganization as a function of shear effects and solvent removal rate during SVA [80,217]. Similar to GISANS, *in situ* RSANS experiments have not been conducted to date due to the measurement time-scales and complex modeling. Additionally, *in situ* RSANS experiments require the design of environmental sample chambers that allow the film to rotate in the beam without affecting the sample or neutron beam path. Overcoming these hurdles can unlock exciting opportunities for high-impact *in situ* neutron scattering.

Figure 11: Schematic of RSANS setup with BCP thin film sample placed on a rotation stage. As the stage rotates, the path of the neutron beam through the sample changes (bottom row), creating a 2D scattering profile for each sample angle. A 3D reciprocal-space scattering intensity map (q_x, q_y, q_z) can be reconstructed from box-averaged q_x slices of each 2D profile of the nanostructured film [212-215].

4. Conclusions and Future Directions

Significant advancements have been made in the characterization of self-assembly in BCP thin films due to the continued development of *in situ* experiments. In particular, *in situ* X-ray and neutron scattering experiments have provided real-time analysis of nanoscale polymer domain reorganization over statistically significant (macroscopic) areas, a powerful and necessary feature of processing-oriented characterization. Additionally, continuous monitoring with *in situ* experimentation ensures that potential *ex situ* effects (*i.e.*, handling of the sample, lag time between experiment and characterization, *etc.*) do not distort analysis of domain restructuring mechanisms. Currently, a multitude of sample geometries (transmission, reflection, grazing-incidence) have been developed for *in situ* X-ray and neutron scattering to probe the in-plane and out-of-plane features in nanostructured thin films, and the resulting insights have greatly improved the design and development of BCP thin film annealing techniques for emerging nanotechnology applications [6,8-11,18,50,218-222]. However, several challenges remain that must be overcome to broaden the impact of *in situ* X-ray and neutron scattering on future BCP-based technologies.

4.1 Improving resolution, reducing data collection time-scales, and advancing scattering tools

Further improvements in scattering resolution at reduced time-scales, and without impacting the nanostructure evolution, are necessary to probe the kinetics of more intricate nanostructure self-assembly effects. For X-rays, this goal refers to reducing beam-induced damage (*e.g.*, polymer crosslinking and/or degradation that affects polymer chain reorganization thermodynamics and kinetics) and enhancing domain contrast during time-resolved experiments [111]. RSoXS and GI-RSoXS offers potential solutions to this challenge by using “soft” (*i.e.*,

low-energy) X-rays, which significantly reduce film damage and increase the contrast between organic domains; however, neither RSoXS nor GI-RSoXS has been employed widely for *in situ* experiments [223]. Additionally, anomalous small-angle X-ray scattering (ASAXS) is an emerging technique that exploits tunable X-ray energies to increase contrast between domains and could prove beneficial for analyzing side chain effects and templated metal deposition [93,121,224,225]. In particular, studies that incorporate these “soft” or resonant X-rays in reflectivity or grazing-incidence geometries will prove beneficial for further exploration of BCP thin films.

For neutron scattering, a key hurdle is the lower neutron flux that results in larger data collection times. Researchers have addressed this problem by improving scattering contrast with selective deuteration and increasing scattering volume with thicker or stacked films [38,53,201-203]; however, kinetic studies still are limited due to large data collection time-scales in comparison to fast reorganization mechanics, especially in ultrathin films ($< \approx 100$ nm). In particular, multidimensional *in situ* analyses (*i.e.* GISANS and RSANS for in-plane and out-of-plane structural and compositional information) have been hindered, in part because data collection times approach several hours for a single experimental condition [208,211]. Reducing the data collection times will require improvements in neutron scattering sources and optics as well as the development of higher-resolution neutron scattering tools. Because the flux from reactor sources is limited for safety reasons, spallation sources offer one opportunity for realizing lower data collection times [226]. Several European countries have combined resources to address this problem with the construction of the ESS, planned to be operational in 2019 [183]. The ESS is an advanced neutron spallation source facility that is expected to increase flux approximately three-fold in comparison to similar existing sources [195]. Another possible

avenue to increased flux is to allow a wider spread of wavelengths in the incident neutron beam. Broadening the incident wavelength spread is generally avoided as greater spreads typically lead to lower resolution; however, new approaches seek to eliminate this resolution issue. For example, the chromatic analysis neutron diffractometer or reflectometer (CANDOR) is being developed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). CANDOR is an NR technique that measures scattering from a broader range of incident wavelengths than traditional NR methods, which reduces measurement time-scales by increasing the incident flux and recording scattering from multiple Q_z values simultaneously [227]. Collecting scattering data from the full range of neutron wavelengths better utilizes the neutron beam and substantially reduces the data collection times during an experiment from hours to seconds [227,228].

In combination with increasing resolution and reducing measurement time-scales, the development of next-generation scattering tools is paramount to advance *in situ* studies of nanostructured films. Several relatively new techniques have been discussed in earlier sections (*e.g.*, RSoXS, CDSAXS, μ GISAXS); however, there are a multitude of other scattering techniques available for use. For example, the multi-angle grazing-incidence k-vector (MAGIK) reflectometer at the NCNR measures specular (in-plane features) and off-specular (out-of-plane features) scattering simultaneously with advanced position sensitive detectors and new data collection methods designed to increase sensitivity and reduce data collection rates [229]. Another potential tool is neutron spin echo (NSE), a time-of-flight scattering technique that measures the change in spin phase after neutrons pass through a sample [183]. With NSE, significantly shorter time-scales can be achieved with the same nanoscale spatial resolution as SANS/SAXS [230]. Furthermore, recent research has demonstrated the ability to measure in-

plane features in thin films with spin echo resolved grazing-incidence scattering (SERGIS) [231,232]. Although there are still challenges associated with the use spin echo techniques with BCP thin films, most notably sample preparation and analysis issues [233], SERGIS offers a promising technique to track interactions between polymer domains [186]. Other scattering tools of potential interest for BCP thin film studies include ultra small-angle X-ray or neutron scattering (USAXS/USANS). Operating at smaller scattering angles than SAXS/SANS, USAXS/USANS (and their grazing-incidence counterparts) [120,234] are capable of measuring larger features than SAXS/SANS, effectively bridging the gap between SAXS/SANS and optical microscopy [235,236]. Additionally, a very small-angle neutron scattering (VSANS) instrument is being built at NIST to cover the size scale ranges from SANS and USANS in a single experiment [237]. Applying USAXS, USANS, and VSANS characterization to the study nanostructured films with larger domains, such as those used for photonic bandgap materials, could prove highly beneficial [238-242].

4.2 Advancing sample chambers and scattering models to progress BCP thin film analysis

The design of state-of-the-art *in situ* sample cell environments is necessary to probe the response of BCP thin films to a wide variety of stimuli. Although several sample environments incorporating control over temperature, solvent exposure, electrical fields, *etc.*, have been designed for X-ray (see section 2.3) and neutron scattering, there are opportunities to develop *in situ* sample chambers for several BCP thin film processing techniques, such as microwave-assisted SVA, magnetic field alignment, and shear alignment. For example, SAXS during magnetic field alignment studies of bulk BCP sample environments potentially could be redesigned for the study of thin films [175,243-245]. Additionally, studies seeking to understand

the mechanistic differences between shear fields induced by manual displacement of a PDMS pad (hard shear) [43-45] and those induced by swelling/deswelling of a PDMS pad adhered to a BCP thin film (soft shear) [46-48] would be notable additions to the field.

More detailed scattering models describing complex restructuring phenomena in advanced scattering setups are required to convert reciprocal q -space measurements into real-space understanding. Although techniques such as GISAXS, RSoXS, GISANS, RSANS, and off-specular scattering are desirable for their ability to investigate multiple dimensions, the complex nature of the techniques and restructuring mechanisms produces scattering patterns that are difficult to interpret and model [51,118,208]. Therefore, it is pivotal that advanced scattering models are developed to extract quantitative information from evolving X-ray and neutron scattering techniques. For example, a new model for a poly(3-hexylthiophene) (P3HT) and surface-functionalized fullerene 1-(3-methyloxycarbonyl) propyl(1-phenyl [6,6]) C₆₁ (PCBM) conjugated polymer bulk heterojunction was constructed to understand the change in morphology before and after thermal annealing to improve photovoltaics performance [246]. Similar model development for nanostructured films would greatly influence our understanding of BCP thin film thermodynamics and kinetics to help design the next-generation of annealing techniques.

4.3 Relating experimental and theoretical/computational results

As the number of *in situ* X-ray and neutron scattering studies continue to grow, experimental results should be linked with theoretical calculations and computational simulations to improve understanding of domain restructuring thermodynamics and kinetics. Additionally, if experimental data can validate simulation/theoretical results, and *vice-versa*, more efficient

means of predicting universal processing conditions can be realized. For example, several models/theories have been developed to probe interfacial effects during thermal annealing [32,33,247-251], solvent vapor annealing [252-258], electrical field alignment [38,259-261], and shear alignment [43,262]. Furthermore, methods to produce scattering profiles from simulation results would allow direct comparisons between theoretical and experimental results [263,264]. For example, Darré *et al.* generated NR profiles for lipid bilayers exposed to water from both molecular dynamics simulations and experimentation [263]. The combined results showed good agreement, which helped validate their simulation studies and detailed the kinetics of lipid bilayer swelling. Thus, connecting *in situ* X-ray and neutron scattering results with theoretical models could greatly enhance the synergistic discovery of more efficient and effective processing conditions for numerous applications.

4.4 Summary

In summary, recent literature has demonstrated how *in situ* X-ray and neutron scattering are powerful characterization techniques that can link kinetic restructuring of nano- and microscale BCP thin film features to thermodynamic and confinement effects over macroscopic areas. Additionally, the insights gleaned from these studies have been applied to the development of more predictive approaches to direct the self-assembly of BCP thin films. However, the need for more refined *in situ* X-ray and neutron scattering experiments continues to grow as the complexity of BCP thin film processing increases (*e.g.*, chemistries, architectures, annealing techniques). Developing appropriate annealing protocols for each BCP thin film system, each with its own set of variables, is nearly impossible without identifying the key parameters of interest. As highlighted in this review, BCP thin films offer a variety of distinct advantages for

emerging nanotechnologies provided improved means of directing their self-assembly can be realized. *In situ* X-ray and neutron scattering approaches offer powerful means for tracking the evolution of nanostructures when subjected to various film deposition and post-processing protocols, thereby uncovering key information into the mechanisms governing restructuring. Therefore, continuing the development of *in situ* X-ray and neutron scattering techniques is paramount to improve the applicability and utility of BCP thin film assemblies in next-generation technologies.

Funding Sources

National Institute of Standards and Technology (NIST – 70NANB12H239)

National Science Foundation (NSF – DMR-1207041)

ACKNOWLEDGMENT

C.K.S. acknowledges support from cooperative agreement 70NANB12H239 from the National Institute of Standards and Technology (NIST), U.S. Department of Commerce as well as support from the National Science Foundation (NSF DMR-1207041) during the writing of this review article. The statements, conclusions, and recommendations are those of the authors and do not necessarily reflect the views of NIST or the U.S. Department of Commerce. T.H.E.

acknowledges support from the Thomas & Kipp Gutshall Professorship during the writing of this review article.

REFERENCES

- [1] F.S. Bates, G.H. Fredrickson, Block copolymers—designer soft materials, *Phys. Today* 52 (1999) 32-38.
- [2] F.S. Bates, Polymer-polymer phase behavior, *Science* 251 (1991) 898-905.
- [3] H. Hu, M. Gopinadhan, C.O. Osuji, Directed self-assembly of block copolymers: a tutorial review of strategies for enabling nanotechnology with soft matter, *Soft Matter* 10 (2014) 3867-3889.
- [4] S.-J. Jeong, J.Y. Kim, B.H. Kim, H.-S. Moon, S.O. Kim, Directed self-assembly of block copolymers for next generation nanolithography, *Mater. Today* 16 (2013) 468-476.
- [5] A. Nunns, J. Gwyther, I. Manners, Inorganic block copolymer lithography, *Polymer* 54 (2013) 1269-1284.
- [6] C.M. Bates, M.J. Maher, D.W. Janes, C.J. Ellison, C.G. Willson, Block copolymer lithography, *Macromolecules* 47 (2013) 2-12.
- [7] J.D. Cushen, C.M. Bates, E.L. Rausch, L.M. Dean, S.X. Zhou, C.G. Willson, C.J. Ellison, Thin film self-assembly of poly(trimethylsilylstyrene-*b*-*d,l*-lactide) with sub-10 nm domains, *Macromolecules* 45 (2012) 8722-8728.
- [8] T.H. Epps, III, R.K. O'Reilly, Block copolymers: controlling nanostructure to generate functional materials - synthesis, characterization, and engineering, *Chem. Sci.* 7 (2016) 1674-1689.
- [9] M.J. Fasolka, A.M. Mayes, Block copolymer thin films: physics and applications, *Annu. Rev. Mater. Sci.* 31 (2001) 323-355.
- [10] R.A. Segalman, Patterning with block copolymer thin films, *Mater. Sci. Eng., R* 48 (2005) 191-226.
- [11] J.N.L. Albert, T.H. Epps, III, Self-assembly of block copolymer thin films, *Mater. Today* 13 (2010) 24-33.
- [12] S. Kim, C.M. Bates, A. Thio, J.D. Cushen, C.J. Ellison, C.G. Willson, F.S. Bates, Consequences of surface neutralization in diblock copolymer thin films, *ACS Nano* 7 (2013) 9905-9919.

- [13] C.M. Bates, T. Seshimo, M.J. Maher, W.J. Durand, J.D. Cushen, L.M. Dean, G. Blachut, C.J. Ellison, C.G. Willson, Polarity-switching top coats enable orientation of sub-10-nm block copolymer domains, *Science* 338 (2012) 775-779.
- [14] X. Zhang, J.F. Douglas, R.L. Jones, Influence of film casting method on block copolymer ordering in thin films, *Soft Matter* 8 (2012) 4980-4987.
- [15] C. Park, C. De Rosa, E.L. Thomas, Large area orientation of block copolymer microdomains in thin films via directional crystallization of a solvent, *Macromolecules* 34 (2001) 2602-2606.
- [16] C. Tang, A. Tracz, M. Kruk, R. Zhang, D.-M. Smilgies, K. Matyjaszewski, T. Kowalewski, Long-range ordered thin films of block copolymers prepared by zone-casting and their thermal conversion into ordered nanostructured carbon, *J. Am. Chem. Soc.* 127 (2005) 6918-6919.
- [17] H. Hu, S. Rangou, M. Kim, P. Gopalan, V. Filiz, A. Avgeropoulos, C.O. Osuji, Continuous equilibrated growth of ordered block copolymer thin films by electrospray deposition, *ACS Nano* 7 (2013) 2960-2970.
- [18] M. Luo, T.H. Epps, III, Directed block copolymer thin film self-assembly: emerging trends in nanopattern fabrication, *Macromolecules* 46 (2013) 7567-7579.
- [19] P.W. Majewski, K.G. Yager, Reordering transitions during annealing of block copolymer cylinder phases, *Soft Matter* 12 (2016) 281-294.
- [20] A. Knoll, A. Horvat, K.S. Lyakhova, G. Krausch, G.J.A. Sevink, A.V. Zvelindovsky, R. Magerle, Phase behavior in thin films of cylinder-forming block copolymers, *Phys. Rev. Lett.* 89 (2002) 035501.
- [21] Y. Tada, H. Yoshida, Y. Ishida, T. Hirai, J.K. Bosworth, E. Dobisz, R. Ruiz, M. Takenaka, T. Hayakawa, H. Hasegawa, Directed self-assembly of POSS containing block copolymer on lithographically defined chemical template with morphology control by solvent vapor, *Macromolecules* 45 (2012) 292-304.
- [22] S. Park, B. Kim, J. Xu, T. Hofmann, B.M. Ocko, T.P. Russell, Lateral ordering of cylindrical microdomains under solvent vapor, *Macromolecules* 42 (2009) 1278-1284.
- [23] J.N.L. Albert, T.D. Bogart, R.L. Lewis, K.L. Beers, M.J. Fasolka, J.B. Hutchison, B.D. Vogt, T.H. Epps, III, Gradient solvent vapor annealing of block copolymer thin films using a microfluidic mixing device, *Nano Lett.* 11 (2011) 1351-1357.
- [24] K.W. Gotrik, C.A. Ross, Solvothermal annealing of block copolymer thin films, *Nano Lett.* 13 (2013) 5117-5122.

- [25] W.I. Park, K. Kim, H.-I. Jang, J.W. Jeong, J.M. Kim, J. Choi, J.H. Park, Y.S. Jung, Directed self-assembly with sub-100 degrees Celsius processing temperature, sub-10 nanometer resolution, and sub-1 minute assembly time, *Small* 8 (2012) 3762-3768.
- [26] E. Kim, H. Ahn, S. Park, H. Lee, M. Lee, S. Lee, T. Kim, E.-A. Kwak, J.H. Lee, X. Lei, J. Huh, J. Bang, B. Lee, D.Y. Ryu, Directed assembly of high molecular weight block copolymers: highly ordered line patterns of perpendicularly oriented lamellae with large periods, *ACS Nano* 7 (2013) 1952-1960.
- [27] X. Zhang, K.D. Harris, N.L.Y. Wu, J.N. Murphy, J.M. Buriak, Fast assembly of ordered block copolymer nanostructures through microwave annealing, *ACS Nano* 4 (2010) 7021-7029.
- [28] D. Borah, M.T. Shaw, J.D. Holmes, M.A. Morris, Sub-10 nm feature size PS-b-PDMS block copolymer structures fabricated by a microwave-assisted solvothermal process, *ACS Appl. Mater. Interfaces* 5 (2013) 2004-2012.
- [29] E.W. Edwards, M.F. Montague, H.H. Solak, C.J. Hawker, P.F. Nealey, Precise control over molecular dimensions of block-copolymer domains using the interfacial energy of chemically nanopatterned substrates, *Adv. Mater.* 16 (2004) 1315-1319.
- [30] E. Han, M. Leolukman, M. Kim, P. Gopalan, Resist free patterning of nonpreferential buffer layers for block copolymer lithography, *ACS Nano* 4 (2010) 6527-6534.
- [31] J.N.L. Albert, M.J. Baney, C.M. Stafford, J.Y. Kelly, T.H. Epps, III, Generation of monolayer gradients in surface energy and surface chemistry for block copolymer thin film studies, *ACS Nano* 3 (2009) 3977-3986.
- [32] C.K. Shelton, T.H. Epps, III, Decoupling substrate surface interactions in block polymer thin film self-assembly, *Macromolecules* 48 (2015) 4572-4580.
- [33] C.K. Shelton, T.H. Epps, III, Mapping substrate surface field propagation in block polymer thin films, *Macromolecules* 49 (2016) 574-580.
- [34] J. Chai, J.M. Buriak, Using cylindrical domains of block copolymers to self-assemble and align metallic nanowires, *ACS Nano* 2 (2008) 489-501.
- [35] X. Shuaigang, Y. XiaoMin, W.E. Erik, L. Young-Hye, F.N. Paul, Graphoepitaxy of cylinder-forming block copolymers for use as templates to pattern magnetic metal dot arrays, *Nanotechnology* 16 (2005) S324.
- [36] I. Bitá, J.K.W. Yang, Y.S. Jung, C.A. Ross, E.L. Thomas, K.K. Berggren, Graphoepitaxy of self-assembled block copolymers on two-dimensional periodic patterned templates, *Science* 321 (2008) 939-943.

- [37] J.Y. Cheng, A.M. Mayes, C.A. Ross, Nanostructure engineering by templated self-assembly of block copolymers, *Nat. Mater.* 3 (2004) 823-828.
- [38] T. Xu, Y. Zhu, S.P. Gido, T.P. Russell, Electric field alignment of symmetric diblock copolymer thin films, *Macromolecules* 37 (2004) 2625-2629.
- [39] V. Olszowka, M. Hund, V. Kuntermann, S. Scherdel, L. Tsarkova, A. Böker, Electric field alignment of a block copolymer nanopattern: direct observation of the microscopic mechanism, *ACS Nano* 3 (2009) 1091-1096.
- [40] P.W. Majewski, M. Gopinadhan, C.O. Osuji, Magnetic field alignment of block copolymers and polymer nanocomposites: scalable microstructure control in functional soft materials, *J. Polym. Sci., Part B: Polym. Phys.* 50 (2012) 2-8.
- [41] T. Thurn-Albrecht, J. Schotter, G.A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C.T. Black, M.T. Tuominen, T.P. Russell, Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates, *Science* 290 (2000) 2126-2129.
- [42] T. Thurn-Albrecht, J. DeRouchey, T.P. Russell, R. Kolb, Pathways toward electric field induced alignment of block copolymers, *Macromolecules* 35 (2002) 8106-8110.
- [43] D.E. Angelescu, J.H. Waller, D.H. Adamson, P. Deshpande, S.Y. Chou, R.A. Register, P.M. Chaikin, Macroscopic orientation of block copolymer cylinders in single-layer films by shearing, *Adv. Mater.* 16 (2004) 1736-1740.
- [44] S. Pujari, M.A. Keaton, P.M. Chaikin, R.A. Register, Alignment of perpendicular lamellae in block copolymer thin films by shearing, *Soft Matter* 8 (2012) 5358-5363.
- [45] S.Y. Kim, A. Nunns, J. Gwyther, R.L. Davis, I. Manners, P.M. Chaikin, R.A. Register, Large-area nanosquare arrays from shear-aligned block copolymer thin films, *Nano Lett.* 14 (2014) 5698-5705.
- [46] M. Luo, D.M. Scott, T.H. Epps, III, Writing highly ordered macroscopic patterns in cylindrical block polymer thin films via raster solvent vapor annealing and soft shear, *ACS Macro Lett.* 4 (2015) 516-520.
- [47] Z. Qiang, L. Zhang, G.E. Stein, K.A. Cavicchi, B.D. Vogt, Unidirectional alignment of block copolymer films induced by expansion of a permeable elastomer during solvent vapor annealing, *Macromolecules* 47 (2014) 1109-1116.
- [48] Z. Qiang, Y. Zhang, J.A. Groff, K.A. Cavicchi, B.D. Vogt, A generalized method for alignment of block copolymer films: solvent vapor annealing with soft shear, *Soft Matter* 10 (2014) 6068-6076.

- [49] J.W. Jeong, Y.H. Hur, H.-j. Kim, J.M. Kim, W.I. Park, M.J. Kim, B.J. Kim, Y.S. Jung, Proximity injection of plasticizing molecules to self-assembling polymers for large-area, ultrafast nanopatterning in the sub-10-nm regime, *ACS Nano* 7 (2013) 6747-6757.
- [50] I.W. Hamley, Ordering in thin films of block copolymers: fundamentals to potential applications, *Prog. Polym. Sci.* 34 (2009) 1161-1210.
- [51] C. Sinturel, M. Vayer, M. Morris, M.A. Hillmyer, Solvent vapor annealing of block polymer thin films, *Macromolecules* 46 (2013) 5399-5415.
- [52] F.S. Bates, M.A. Hillmyer, T.P. Lodge, C.M. Bates, K.T. Delaney, G.H. Fredrickson, Multiblock polymers: panacea or pandora's box?, *Science* 336 (2012) 434-440.
- [53] C.K. Shelton, R.L. Jones, J.A. Dura, T.H. Epps, III, Tracking solvent distribution in block polymer thin films with in situ solvent vapor annealing during neutron scattering, *ACS Nano* under review (2016).
- [54] M.J. Heinzer, S. Han, J.A. Pople, D.G. Baird, S.M. Martin, In situ tracking of microstructure spacing and ordered domain compression during the drying of solution-cast block copolymer films using small-angle X-ray scattering, *Macromolecules* 45 (2012) 3480-3486.
- [55] W. Bai, K.G. Yager, C.A. Ross, In situ characterization of the self-assembly of a polystyrene-polydimethylsiloxane block copolymer during solvent vapor annealing, *Macromolecules* 48 (2015) 8574-8584.
- [56] P. Zhang, H. Huang, D. Yan, T. He, In situ study of the breakout crystallization in the poly(butadiene)-block-poly(ϵ -caprolactone) thin film, *Langmuir* 28 (2012) 6419-6427.
- [57] G. Coulon, B. Collin, D. Ausserre, D. Chatenay, T.P. Russell, Islands and holes on the free-surface of thin diblock copolymer films .I. characteristics of formation and growth, *J. Phys. France* 51 (1990) 2801-2811.
- [58] L. Tsarkova, A. Horvat, G. Krausch, A.V. Zvelindovsky, G.J.A. Sevink, R. Magerle, Defect evolution in block copolymer thin films via temporal phase transitions, *Langmuir* 22 (2006) 8089-8095.
- [59] A. Horvat, G.J.A. Sevink, A.V. Zvelindovsky, A. Krekhov, L. Tsarkova, Specific features of defect structure and dynamics in the cylinder phase of block copolymers, *ACS Nano* 2 (2008) 1143-1152.
- [60] L. Tsarkova, A. Knoll, R. Magerle, Rapid transitions between defect configurations in a block copolymer melt, *Nano Lett.* 6 (2006) 1574-1577.

- [61] N.A. Yufa, J. Li, S.J. Sibener, In-situ high-temperature studies of diblock copolymer structural evolution, *Macromolecules* 42 (2009) 2667-2671.
- [62] J.K. Hobbs, N. Mullin, C.H.M. Weber, O.E. Farrance, C. Vasilev, 'Watching' processes in soft matter with SPM, *Mater. Today* 12 (2009) 26-33.
- [63] Recent advances in anionic polymerization, in: T.E. Hogen-Esch, J. Smid (Eds.) *International Symposium on Recent Advances in Anionic Polymerization*, Elsevier Science Publishing Co., Inc., New York, New York, 1986, p. 468.
- [64] J.K. Hobbs, R.A. Register, Imaging block copolymer crystallization in real time with the atomic force microscope, *Macromolecules* 39 (2006) 703-710.
- [65] G. Reiter, G. Castelein, J.-U. Sommer, A. Röttele, T. Thurn-Albrecht, Direct visualization of random crystallization and melting in arrays of nanometer-size polymer crystals, *Phys. Rev. Lett.* 87 (2001) 226101.
- [66] V. Olszowka, M. Hund, V. Kuntermann, S. Scherdel, L. Tsarkova, A. Boker, G. Krausch, Large scale alignment of a lamellar block copolymer thin film via electric fields: a time-resolved SFM study, *Soft Matter* 2 (2006) 1089-1094.
- [67] A. Knoll, R. Magerle, G. Krausch, Phase behavior in thin films of cylinder-forming ABA block copolymers: experiments, *J. Chem. Phys.* 120 (2004) 1105-1116.
- [68] A. Horvat, A. Knoll, G. Krausch, L. Tsarkova, K.S. Lyakhova, G.J.A. Sevink, A.V. Zvelindovsky, R. Magerle, Time evolution of surface relief structures in thin block copolymer films, *Macromolecules* 40 (2007) 6930-6939.
- [69] A. Knoll, K.S. Lyakhova, A. Horvat, G. Krausch, G.J.A. Sevink, A.V. Zvelindovsky, R. Magerle, Direct imaging and mesoscale modelling of phase transitions in a nanostructured fluid, *Nat. Mater.* 3 (2004) 886-891.
- [70] C. Xu, X. Fu, M. Fryd, S. Xu, B.B. Wayland, K.I. Winey, R.J. Composto, Reversible stimuli-responsive nanostructures assembled from amphiphilic block copolymers, *Nano Lett.* 6 (2006) 282-287.
- [71] L. Tsarkova, G.J.A. Sevink, G. Krausch, Nanopattern evolution in block copolymer films: experiment, simulations and challenges, in: E.A.H. Müller, H.-W. Schmidt (Eds.), *Complex macromolecular systems I*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 33-73.
- [72] N.L.Y. Wu, K.D. Harris, J.M. Buriak, Conversion of bilayers of PS-b-PDMS block copolymer into closely packed, aligned silica nanopatterns, *ACS Nano* 7 (2013) 5595-5606.

- [73] C. Sinturel, D. Grosso, M. Boudot, H. Amenitsch, M.A. Hillmyer, A. Pineau, M. Vayer, Structural transitions in asymmetric poly(styrene)-block-poly(lactide) thin films induced by solvent vapor exposure, *ACS Appl. Mater. Interfaces* 6 (2014) 12146-12152.
- [74] B. Rippner, K. Boschkova, P.M. Claesson, T. Arnebrant, Interfacial films of poly(ethylene oxide)–poly(butylene oxide) block copolymers characterized by disjoining pressure measurements, in situ ellipsometry, and surface tension measurements, *Langmuir* 18 (2002) 5213-5221.
- [75] Z. Qiang, J. Xue, K.A. Cavicchi, B.D. Vogt, Morphology control in mesoporous carbon films using solvent vapor annealing, *Langmuir* 29 (2013) 3428-3438.
- [76] P. Mokarian-Tabari, T.W. Collins, J.D. Holmes, M.A. Morris, Cyclical “flipping” of morphology in block copolymer thin films, *ACS Nano* 5 (2011) 4617-4623.
- [77] J. Gensel, C. Liedel, H.G. Schoberth, L. Tsarkova, "Micro-structure-macro-response" relationship in swollen block copolymer films, *Soft Matter* 5 (2009) 2534-2537.
- [78] K. Fukunaga, T. Hashimoto, H. Elbs, G. Krausch, Self-assembly of a lamellar ABC triblock copolymer thin film, *Macromolecules* 35 (2002) 4406-4413.
- [79] H. Elbs, G. Krausch, Ellipsometric determination of Flory-Huggins interaction parameters in solution, *Polymer* 45 (2004) 7935-7942.
- [80] J.N.L. Albert, W.-S. Young, R.L. Lewis, T.D. Bogart, J.R. Smith, T.H. Epps, III, Systematic study on the effect of solvent removal rate on the morphology of solvent vapor annealed ABA triblock copolymer thin films, *ACS Nano* 6 (2012) 459-466.
- [81] V. Olszowka, L. Tsarkova, A. Boker, 3-Dimensional control over lamella orientation and order in thick block copolymer films, *Soft Matter* 5 (2009) 812-819.
- [82] U. Zettl, A. Knoll, L. Tsarkova, Effect of confinement on the mesoscale and macroscopic swelling of thin block copolymer films, *Langmuir* 26 (2010) 6610-6617.
- [83] A. Jo, G.H. Gu, H.C. Moon, S.H. Han, S.H. Oh, C.G. Park, J.K. Kim, In situ TEM observation of phase transition of the nanoscopic patterns on baroplastic block copolymer films during nanoindentation, *Nanoscale* 5 (2013) 4351-4354.
- [84] H. Liem, L.Y. Yeung, Segment self-orientational behavior in shape memory polymer thin films probed by raman spectroscopy, *J. Appl. Polym. Sci.* 105 (2007) 765-770.
- [85] T.P. Russell, X-ray and neutron reflectivity for the investigation of polymers, *Mater. Sci. Rep.* 5 (1990) 171-271.

- [86] M. Tolan, X-ray scattering from soft-matter thin films, Springer-Verlag Berlin Heidelberg, 1999.
- [87] B. Hammouda, Probing nanoscale structures: the sans toolbox, NIST, 2008.
- [88] J.S. Higgins, H. Benoît, Polymers and neutron scattering, Clarendon Press, 1994.
- [89] V.K. Peterson, C.M. Papadakis, Functional materials analysis using in situ and in operando X-ray and neutron scattering, *IUCrJ* 2 (2015) 292-304.
- [90] R. Pynn, Neutron scattering: a primer, *Los Alamos Science* 19 (1990) 1-31.
- [91] W.G. Stirling, C. Vettier, The most useful microscopic probes - neutrons and synchrotron X-rays, *Neutron News* 21 (2010) 13-17.
- [92] T. Lodge, Characterization of polymer materials by scattering techniques, with applications to block copolymers, *Microchim. Acta* 116 (1994) 1-31.
- [93] S. Sakurai, Recent developments in polymer applications of synchrotron small-angle X-ray scattering, *Polym. Int.* (2016) 5136.
- [94] D.S. Sivia, Elementary scattering theory: for X-ray and neutron users, OUP Oxford, 2011.
- [95] N. Stribeck, X-ray scattering of soft matter, Springer Berlin Heidelberg, 2007.
- [96] G.E. Stein, Scattering techniques for thin polymer films, *Functional polymer films*, Wiley-VCH Verlag GmbH & Co. KGaA 2011, pp. 669-694.
- [97] M.A. Graewert, D.I. Svergun, Impact and progress in small and wide angle X-ray scattering (SAXS and WAXS), *Curr. Opin. Struc. Biol.* 23 (2013) 748-754.
- [98] S. Guldin, Inorganic nanoarchitectures by organic self-assembly, Springer International Publishing, 2013.
- [99] Argonne National Laboratory, APS small angle X-ray scattering (SAXS) beamlines. <http://small-angle.aps.anl.gov/aps_beam_lines.html>).
- [100] K.O. Stuen, C. Liu, A.M. Welander, G. Liu, J.J. de Pablo, P.F. Nealey, D.K. Satapathy, K. Nygård, O. Bunk, H.H. Solak, J.F. van der Veen, In situ characterization of block copolymer ordering on chemically nanopatterned surfaces by time-resolved small angle X-ray scattering, *J. Vac. Sci. Technol., B* 26 (2008) 2504-2508.

- [101] G. Liu, S.P. Delcambre, K.O. Stuen, G.S.W. Craig, J.J. De Pablo, Mechanism and dynamics of block copolymer directed assembly with density multiplication on chemically patterned surfaces, *J. Vac. Sci. Technol., B* 28 (2010) C6B13-C6B19.
- [102] K.P. Mineart, B. Lee, R.J. Spontak, A solvent-vapor approach toward the control of block ionomer morphologies, *Macromolecules* 49 (2016) 3126-3137.
- [103] C. Liedel, C.W. Pester, M. Ruppel, C. Lewin, M.J. Pavan, V.S. Urban, R. Shenhar, P. Bösecke, A. Böker, Block copolymer nanocomposites in electric fields: kinetics of alignment, *ACS Macro Lett.* 2 (2013) 53-58.
- [104] A. Böker, K. Schmidt, A. Knoll, H. Zettl, H. Hänsel, V. Urban, V. Abetz, G. Krausch, The influence of incompatibility and dielectric contrast on the electric field-induced orientation of lamellar block copolymers, *Polymer* 47 (2006) 849-857.
- [105] M.J. Heinzer, S. Han, J.A. Pople, D.G. Baird, S.M. Martin, In situ measurement of block copolymer ordering kinetics during the drying of solution-cast films using small-angle X-ray scattering, *Macromolecules* 45 (2012) 3471-3479.
- [106] C. Stegelmeier, A. Exner, S. Hauschild, V. Filiz, J. Perlich, S.V. Roth, V. Abetz, S. Förster, Evaporation-induced block copolymer self-assembly into membranes studied by in situ synchrotron SAXS, *Macromolecules* 48 (2015) 1524-1530.
- [107] W. Zhao, F. Liu, X. Wei, D. Chen, G.M. Grason, T.P. Russell, Formation of H* phase in chiral block copolymers: morphology evolution as revealed by time-resolved X-ray scattering, *Macromolecules* 46 (2013) 474-483.
- [108] R.J. Albalak, M.S. Capel, E.L. Thomas, Solvent swelling of roll-cast triblock copolymer films, *Polymer* 39 (1998) 1647-1656.
- [109] W. Gu, J. Huh, S.W. Hong, B.R. Sveinbjornsson, C. Park, R.H. Grubbs, T.P. Russell, Self-assembly of symmetric brush diblock copolymers, *ACS Nano* 7 (2013) 2551-2558.
- [110] J. DeRouchey, T. Thurn-Albrecht, T.P. Russell, R. Kolb, Block copolymer domain reorientation in an electric field: an in-situ small-angle X-ray scattering study, *Macromolecules* 37 (2004) 2538-2543.
- [111] S.A. Vaselabadi, D. Shakerisaz, P. Ruchhoeft, J. Strzalka, G.E. Stein, Radiation damage in polymer films from grazing-incidence X-ray scattering measurements, *J. Polym. Sci., Part B: Polym. Phys.* (2016) 1074-1086.

- [112] J.M. Virgili, Y. Tao, J.B. Kortright, N.P. Balsara, R.A. Segalman, Analysis of order formation in block copolymer thin films using resonant soft X-ray scattering, *Macromolecules* 40 (2007) 2092-2099.
- [113] E. Pavlopoulou, S.H. Anastasiadis, J.B. Kortright, W. Bras, G. Portale, Investigation of the micellization in thin films using resonant soft X-ray scattering, *IOP Conf. Ser.: Mater. Sci. Eng.* 14 (2010) 012017.
- [114] C. Wang, D.H. Lee, A. Hexemer, M.I. Kim, W. Zhao, H. Hasegawa, H. Ade, T.P. Russell, Defining the nanostructured morphology of triblock copolymers using resonant soft X-ray scattering, *Nano Lett.* 11 (2011) 3906-3911.
- [115] A. Harald, W. Cheng, Y. Hongping, The case for soft X-rays: improved compositional contrast for structure and morphology determination with real and reciprocal space methods, *IOP Conf. Ser.: Mater. Sci. Eng.* 14 (2010) 012020.
- [116] C.F. Welch, R.P. Hjelm, J.T. Mang, M.E. Hawley, D.A. Wroblewski, E. Bruce Orler, J.B. Kortright, Resonant soft X-ray scattering and reflectivity study of the phase-separated structure of thin poly(styrene-*b*-methyl methacrylate) films, *J. Polym. Sci., Part B: Polym. Phys.* 51 (2013) 149-157.
- [117] D.T. Wong, C. Wang, K.M. Beers, J.B. Kortright, N.P. Balsara, Mesoporous block copolymer morphology studied by contrast-matched resonant soft X-ray scattering, *Macromolecules* 45 (2012) 9188-9195.
- [118] J.H. Carpenter, A. Hunt, H. Ade, Characterizing morphology in organic systems with resonant soft X-ray scattering, *J. Electron. Spectrosc. Relat. Phenom.* 200 (2015) 2-14.
- [119] P. Müller-Buschbaum, A basic introduction to grazing incidence small-angle X-ray scattering, in: M. Gomez, A. Nogales, C.M. Garcia-Gutierrez, T.A. Ezquerra (Eds.), *Applications of synchrotron light to scattering and diffraction in materials and life sciences*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009, pp. 61-89.
- [120] P. Müller-Buschbaum, Grazing incidence small-angle X-ray scattering: an advanced scattering technique for the investigation of nanostructured polymer films, *Anal. Bioanal. Chem.* 376 (2003) 3-10.
- [121] A. Hexemer, P. Muller-Buschbaum, Advanced grazing-incidence techniques for modern soft-matter materials analysis, *IUCrJ* 2 (2015) 106-125.
- [122] B. Lee, I. Park, J. Yoon, S. Park, J. Kim, K.-W. Kim, T. Chang, M. Ree, Structural analysis of block copolymer thin films with grazing incidence small-angle X-ray scattering, *Macromolecules* 38 (2005) 4311-4323.

- [123] P. Müller-Buschbaum, GISAXS and GISANS as metrology technique for understanding the 3D morphology of block copolymer thin films, *Eur. Polym. J.*, in print.
- [124] S. Sasaki, H. Masunaga, H. Tajiri, K. Inoue, H. Okuda, H. Noma, K. Honda, A. Takahara, M. Takata, In situ investigation of annealing effect on lamellar stacking structure of polyethylene thin films by synchrotron grazing-incidence small-angle and wide-angle X-ray scattering, *J. Appl. Crystallogr.* 40 (2007) s642-s644.
- [125] E. Kim, S. Choi, R. Guo, D.Y. Ryu, C.J. Hawker, T.P. Russell, Transition behavior of PS-b-PMMA films on the balanced interfacial interactions, *Polymer* 51 (2010) 6313-6318.
- [126] N. Torikai, N.L. Yamada, D. Kawaguchi, A. Takano, Y. Matsushita, E. Watkins, J.P. Majewski, H. Okuda, In-situ reflectometry observation on structural changes of thin self-assembled block copolymer films, *J. Phys. Conf. Ser.* 83 (2007) 012028.
- [127] C. Shin, D.Y. Ryu, J. Huh, J.H. Kim, K.-W. Kim, Order-to-order transitions of block copolymer in film geometry, *Macromolecules* 42 (2009) 2157-2160.
- [128] A. Sepe, E.T. Hoppe, S. Jaksch, D. Magerl, Q. Zhong, J. Perlich, D. Posselt, D.M. Smilgies, C.M. Papadakis, The effect of heat treatment on the internal structure of nanostructured block copolymer films, *J. Phys.: Condens. Matter* 23 (2011) 254213.
- [129] J. Jung, H.-W. Park, S. Lee, H. Lee, T. Chang, K. Matsunaga, H. Jinnai, Effect of film thickness on the phase behaviors of diblock copolymer thin film, *ACS Nano* 4 (2010) 3109-3116.
- [130] E. Kim, H. Ahn, D.Y. Ryu, J. Kim, J. Cho, Transition behavior of weakly interacting PS-b-PMMA films on preferential surfaces: a direct observation by GISAXS, *Macromolecules* 42 (2009) 8385-8391.
- [131] J. He, R. Tangirala, T. Emrick, T.P. Russell, A. Böker, X. Li, J. Wang, Self-assembly of nanoparticle-copolymer mixtures: a kinetic point of view, *Adv. Mater.* 19 (2007) 381-385.
- [132] M. Maret, R. Tiron, X. Chevalier, P. Gergaud, A. Gharbi, C. Lapeyre, J. Pradelles, V. Jousseume, G. Fleury, G. Hadziioannou, N. Boudet, C. Navarro, Probing self-assembly of cylindrical morphology block copolymer using in situ and ex situ grazing incidence small-angle X-ray scattering: the attractive case of graphoepitaxy, *Macromolecules* 47 (2014) 7221-7229.
- [133] X. Gu, I. Gunkel, A. Hexemer, T.P. Russell, Controlling domain spacing and grain size in cylindrical block copolymer thin films by means of thermal and solvent vapor annealing, *Macromolecules* 49 (2016) 3373-3381.

- [134] Y. Kamata, A.J. Parnell, P. Gutfreund, M.W.A. Skoda, A.J.C. Dennison, R. Barker, S. Mai, J.R. Howse, A.J. Ryan, N. Torikai, M. Kawaguchi, R.A.L. Jones, Hydration and ordering of lamellar block copolymer films under controlled water vapor, *Macromolecules* 47 (2014) 8682-8690.
- [135] Z. Di, D. Posselt, D.-M. Smilgies, C.M. Papadakis, Structural rearrangements in a lamellar diblock copolymer thin film during treatment with saturated solvent vapor, *Macromolecules* 43 (2010) 418-427.
- [136] J. Zhang, D. Posselt, D.-M. Smilgies, J. Perlich, K. Kyriakos, S. Jaksch, C.M. Papadakis, Lamellar diblock copolymer thin films during solvent vapor annealing studied by GISAXS: different behavior of parallel and perpendicular lamellae, *Macromolecules* 47 (2014) 5711-5718.
- [137] X. Gu, I. Gunkel, A. Hexemer, T.P. Russell, Solvent vapor annealing of block copolymer thin films: removal of processing history, *Colloid. Polym. Sci.* 292 (2014) 1795-1802.
- [138] K.A. Cavicchi, K.J. Berthiaume, T.P. Russell, Solvent annealing thin films of poly(isoprene-*b*-lactide), *Polymer* 46 (2005) 11635-11639.
- [139] Z. Di, D. Posselt, D.-M. Smilgies, R. Li, M. Rauscher, I.I. Potemkin, C.M. Papadakis, Stepwise swelling of a thin film of lamellae-forming poly(styrene-*b*-butadiene) in cyclohexane vapor, *Macromolecules* 45 (2012) 5185-5195.
- [140] C.M. Papadakis, Z. Di, D. Posselt, D.-M. Smilgies, Structural instabilities in lamellar diblock copolymer thin films during solvent vapor uptake, *Langmuir* 24 (2008) 13815-13818.
- [141] A. Sepe, P. Černoš, P. Štěpánek, E.T. Hoppe, C.M. Papadakis, Creation of lateral structures in diblock copolymer thin films during vapor uptake and subsequent drying – effect of film thickness, *Eur. Polym. J.* 50 (2014) 87-96.
- [142] J. Zhang, D. Posselt, A. Sepe, X. Shen, J. Perlich, D.-M. Smilgies, C.M. Papadakis, Structural evolution of perpendicular lamellae in diblock copolymer thin films during solvent vapor treatment investigated by grazing-incidence small-angle X-ray scattering, *Macromol. Rapid Commun.* 34 (2013) 1289-1295.
- [143] X. Ting, J.M. Matthew, K. Seunghyun, D.S. James, G. Oleg, O. Ben, P.R. Thomas, Selective solvent-induced reversible surface reconstruction of diblock copolymer thin films, *New polym. Mat.*, American Chemical Society, 2005, pp. 158-170.
- [144] S.H. Kim, M.J. Misner, T. Xu, M. Kimura, T.P. Russell, Highly oriented and ordered arrays from block copolymers via solvent evaporation, *Adv. Mater.* 16 (2004) 226-231.

- [145] B. Ahn, W. Kwon, H. Kim, M. Ree, Cooperative and selective self-assembly behaviors of diblock copolypeptides in nanoscale thin films, *Polym. Chem.* 5 (2014) 1912-1922.
- [146] M. Komura, H. Komiyama, K. Nagai, T. Iyoda, Direct observation of faceted grain growth of hexagonal cylinder domains in a side chain liquid crystalline block copolymer matrix, *Macromolecules* 46 (2013) 9013-9020.
- [147] Y.Y. Kim, B. Ahn, S. Sa, M. Jeon, S.V. Roth, S.Y. Kim, M. Ree, Self-assembly characteristics of a crystalline–amorphous diblock copolymer in nanoscale thin films, *Macromolecules* 46 (2013) 8235-8244.
- [148] Y. Rho, C. Kim, T. Higashihara, S. Jin, J. Jung, T.J. Shin, A. Hirao, M. Ree, Complex self-assembled morphologies of thin films of an asymmetric $A_3B_3C_3$ star polymer, *ACS Macro Lett.* 2 (2013) 849-855.
- [149] C. Shin, H. Ahn, E. Kim, D.Y. Ryu, J. Huh, K.-W. Kim, T.P. Russell, Transition behavior of block copolymer thin films on preferential surfaces, *Macromolecules* 41 (2008) 9140-9145.
- [150] S.H. Kim, M.J. Misner, L. Yang, O. Gang, B.M. Ocko, T.P. Russell, Salt complexation in block copolymer thin films, *Macromolecules* 39 (2006) 8473-8479.
- [151] E. Kim, H. Ahn, H. Lee, B. Lee, D.Y. Ryu, Ordering and microdomain orientation in block copolymer films by thermal deprotection, *Polymer* 52 (2011) 2677-2684.
- [152] S.H. Kim, M.J. Misner, T.P. Russell, Controlling orientation and order in block copolymer thin films, *Adv. Mater.* 20 (2008) 4851-4856.
- [153] M.A. Chavis, D.-M. Smilgies, U.B. Wiesner, C.K. Ober, Widely tunable morphologies in block copolymer thin films through solvent vapor annealing using mixtures of selective solvents, *Adv. Funct. Mater.* 25 (2015) 3057-3065.
- [154] M.Y. Paik, J.K. Bosworth, D.-M. Smilgies, E.L. Schwartz, X. Andre, C.K. Ober, Reversible morphology control in block copolymer films via solvent vapor processing: an in situ GISAXS study, *Macromolecules* 43 (2010) 4253-4260.
- [155] K.A. Cavicchi, T.P. Russell, Solvent annealed thin films of asymmetric polyisoprene–polylactide diblock copolymers, *Macromolecules* 40 (2007) 1181-1186.
- [156] I. Gunkel, X. Gu, Z. Sun, E. Schaible, A. Hexemer, T.P. Russell, An in situ GISAXS study of selective solvent vapor annealing in thin block copolymer films: symmetry breaking of in-plane sphere order upon deswelling, *J. Polym. Sci., Part B: Polym. Phys.* 54 (2015) 331-338.

- [157] X. Gu, I. Gunkel, A. Hexemer, W. Gu, T.P. Russell, An in situ grazing incidence X-ray scattering study of block copolymer thin films during solvent vapor annealing, *Adv. Mater.* 26 (2014) 273-281.
- [158] E.B. Gowd, B. Marcus, S. Manfred, In situ GISAXS study on solvent vapour induced orientation switching in PS-b-P4VP block copolymer thin films, *IOP Conf. Ser.: Mater. Sci. Eng.* 14 (2010) 012015.
- [159] P. Müller-Buschbaum, S.V. Roth, M. Burghammer, A. Diethert, P. Panagiotou, C. Riekel, Multiple-scaled polymer surfaces investigated with micro-focus grazing-incidence small-angle X-ray scattering, *Europhys. Lett.* 61 (2003) 639.
- [160] V. Körstgens, J. Wiedersich, R. Meier, J. Perlich, S.V. Roth, R. Gehrke, P. Müller-Buschbaum, Combining imaging ellipsometry and grazing incidence small angle X-ray scattering for in situ characterization of polymer nanostructures, *Anal. Bioanal. Chem.* 396 (2010) 139-149.
- [161] M.M. Abul Kashem, G. Kaune, A. Diethert, W. Wang, K. Schlage, S. Couet, R. Röhlberger, S.V. Roth, P. Müller-Buschbaum, Selective doping of block copolymer nanodomains by sputter deposition of iron, *Macromolecules* 44 (2011) 1621-1627.
- [162] M.A. Hillmyer, Nanoporous materials from block copolymer precursors, in: V. Abetz (Ed.), *Block copolymers II*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, pp. 137-181.
- [163] M.J. Misner, H. Skaff, T. Emrick, T.P. Russell, Directed deposition of nanoparticles using diblock copolymer templates, *Adv. Mater.* 15 (2003) 221-224.
- [164] S.-J. Jeong, G. Xia, B.H. Kim, D.O. Shin, S.-H. Kwon, S.-W. Kang, S.O. Kim, Universal block copolymer lithography for metals, semiconductors, ceramics, and polymers, *Adv. Mater.* 20 (2008) 1898-1904.
- [165] J.Y. Cheng, C.A. Ross, V.Z.H. Chan, E.L. Thomas, R.G.H. Lammertink, G.J. Vancso, Formation of a cobalt magnetic dot array via block copolymer lithography, *Adv. Mater.* 13 (2001) 1174-1178.
- [166] S. Park, J.-Y. Wang, B. Kim, J. Xu, T.P. Russell, A simple route to highly oriented and ordered nanoporous block copolymer templates, *ACS Nano* 2 (2008) 766-772.
- [167] D.F. Sunday, M.R. Hammond, C. Wang, W.-I. Wu, R.J. Kline, G.E. Stein, Three-dimensional X-ray metrology for block copolymer lithography line-space patterns, *MOEMS* 12 (2013) 031103-031103.

- [168] I. Saito, T. Miyazaki, K. Yamamoto, Depth-resolved structure analysis of cylindrical microdomain in block copolymer thin film by grazing-incidence small-angle X-ray scattering utilizing low-energy X-rays, *Macromolecules* 48 (2015) 8190-8196.
- [169] I. Saito, D. Shimada, M. Aikawa, T. Miyazaki, K. Shimokita, H. Takagi, K. Yamamoto, Orientation and relaxation behaviors of lamellar microdomains of poly(methyl methacrylate)-b-poly(n-butyl acrylate) thin films as revealed by grazing-incidence small-angle X-ray scattering, *Polym. J.* 48 (2016) 399-406.
- [170] R.L. Jones, T. Hu, E.K. Lin, W.-L. Wu, R. Kolb, D.M. Casa, P.J. Bolton, G.G. Barclay, Small angle X-ray scattering for sub-100 nm pattern characterization, *Appl. Phys. Lett.* 83 (2003) 4059-4061.
- [171] R.L. Jones, T. Hu, C.L. Soles, E.K. Lin, R.M. Reano, S.W. Pang, D.M. Casa, Real-time shape evolution of nanoimprinted polymer structures during thermal annealing, *Nano Lett.* 6 (2006) 1723-1728.
- [172] S. Knight, R. Dixon, R.L. Jones, E.K. Lin, N.G. Orji, R. Silver, J.S. Villarrubia, A.E. Vladár, W.-l. Wu, Advanced metrology needs for nanoelectronics lithography, *C. R. Phys.* 7 (2006) 931-941.
- [173] D.F. Sunday, M.R. Hammond, C. Wang, W.-l. Wu, D.M. DeLongchamp, M. Tjio, J.Y. Cheng, J.W. Pitera, R.J. Kline, Determination of the internal morphology of nanostructures patterned by directed self assembly, *ACS Nano* 8 (2014) 8426-8437.
- [174] M.A. Singh, M.N. Groves, M.S. Müller, I.J. Stahlbrand, D.-M. Smilgies, Thermal quenching sample chamber for grazing incidence small angle X-ray scattering studies of polymer films, *Rev. Sci. Instrum.* 78 (2007) 113910.
- [175] Y. Rokhlenko, M. Gopinadhan, C.O. Osuji, K. Zhang, C.S. O'Hern, S.R. Larson, P. Gopalan, P.W. Majewski, K.G. Yager, Magnetic alignment of block copolymer microdomains by intrinsic chain anisotropy, *Phys. Rev. Lett.* 115 (2015) 258302.
- [176] J.-Y. Liou, Y.-S. Sun, Tailor-made dimensions of diblock copolymer truncated micelles on a solid by UV irradiation, *Soft Matter* 11 (2015) 7119-7129.
- [177] E. Metwalli, V. Körstgens, K. Schlage, R. Meier, G. Kaune, A. Buffet, S. Couet, S.V. Roth, R. Röhlberger, P. Müller-Buschbaum, Cobalt nanoparticles growth on a block copolymer thin film: a time-resolved GISAXS study, *Langmuir* 29 (2013) 6331-6340.
- [178] E. Metwalli, J.F. Moulin, J. Perlich, W. Wang, A. Diethert, S.V. Roth, P. Müller-Buschbaum, Polymer-template-assisted growth of gold nanowires using a novel flow-stream technique, *Langmuir* 25 (2009) 11815-11821.

- [179] E. Metwalli, S. Couet, K. Schlage, R. Röhlberger, V. Körstgens, M. Ruderer, W. Wang, G. Kaune, S.V. Roth, P. Müller-Buschbaum, In situ GISAXS investigation of gold sputtering onto a polymer template, *Langmuir* 24 (2008) 4265-4272.
- [180] S.V. Roth, G. Santoro, J.F.H. Risch, S. Yu, M. Schwartzkopf, T. Boese, R. Döhrmann, P. Zhang, B. Besner, P. Bremer, D. Rukser, M.A. Rübhausen, N.J. Terrill, P.A. Staniec, Y. Yao, E. Metwalli, P. Müller-Buschbaum, Patterned diblock co-polymer thin films as templates for advanced anisotropic metal nanostructures, *ACS Appl. Mater. Interfaces* 7 (2015) 12470-12477.
- [181] K. Schlage, S. Couet, S.V. Roth, U. Vainio, R. Rüffer, M.M.A. Kashem, P. Müller-Buschbaum, R. Röhlberger, The formation and magnetism of iron nanostructures on ordered polymer templates, *New J. Phys.* 14 (2012) 043007.
- [182] R. Döhrmann, S. Botta, A. Buffet, G. Santoro, K. Schlage, M. Schwartzkopf, S. Bommel, J.F.H. Risch, R. Mannweiler, S. Brunner, E. Metwalli, P. Müller-Buschbaum, S.V. Roth, A new highly automated sputter equipment for in situ investigation of deposition processes with synchrotron radiation, *Rev. Sci. Instrum.* 84 (2013) 043901.
- [183] T. Imae, T. Kanaya, M. Furusaka, N. Torikai, *Neutrons in soft matter*, Wiley, 2011.
- [184] J.M. Virgili, A.J. Nedoma, R.A. Segalman, N.P. Balsara, Ionic liquid distribution in ordered block copolymer solutions, *Macromolecules* 43 (2010) 3750-3756.
- [185] E. Sivaniah, R.A.L. Jones, D. Higgins, Small molecule segregation at polymer interfaces, *Macromolecules* 42 (2009) 8844-8850.
- [186] N. Torikai, N.L. Yamada, A. Noro, M. Harada, D. Kawaguchi, A. Takano, Y. Matsushita, Neutron reflectometry on interfacial structures of the thin films of polymer and lipid, *Polym. J.* 39 (2007) 1238-1246.
- [187] A.J. Jackson, *Introduction to small-angle neutron scattering and neutron reflectometry*, NIST Center for Neutron Research, Gaithersburg, MD, 2008.
- [188] R. Pynn, Neutron scattering—a non-destructive microscope for seeing inside matter, in: L. Liang, R. Rinaldi, H. Schober (Eds.), *Neutron applications in earth, energy and environmental sciences*, Springer US, Boston, MA, 2009, pp. 15-36.
- [189] T.P. Russell, P. Lambooy, J.G. Barker, P. Gallagher, S.K. Satija, G.J. Kellogg, A.M. Mayes, Small angle neutron scattering studies on ultrathin films, *Macromolecules* 28 (1995) 787-789.
- [190] Report on the status and needs of major neutron scattering facilities and instruments in the united states, Office of Science and Technology Policy, Washington D.C., 2002.

- [191] Free electron lasers and other advanced sources of light: scientific research opportunities, The National Academies Press, Washington, DC, 1994.
- [192] D. Castelvechi, Next-generation X-ray source fires up, *Nature* 526 (2015) 15-16.
- [193] T. Worlton, R. Osborn, Neutron scattering facilities. <<http://www.neutron.anl.gov/facilities.html>>, 2013.
- [194] U.S. Department of Energy: Office of Science, Neutron scattering facilities: high flux isotope reactor (HFIR). <<http://science.energy.gov/bes/suf/user-facilities/neutron-scattering-facilities/hfir/>>, 2015.
- [195] European spallation source activity report 2015, European Spallation Source, Lund, Sweden, 2015.
- [196] E. Huang, T.P. Russell, C. Harrison, P.M. Chaikin, R.A. Register, C.J. Hawker, J. Mays, Using surface active random copolymers to control the domain orientation in diblock copolymer thin films, *Macromolecules* 31 (1998) 7641-7650.
- [197] T. Xu, C.J. Hawker, T.P. Russell, Interfacial interaction dependence of microdomain orientation in diblock copolymer thin films, *Macromolecules* 38 (2005) 2802-2805.
- [198] G.J. Kellogg, D.G. Walton, A.M. Mayes, P. Lambooy, T.P. Russell, P.D. Gallagher, S.K. Satija, Observed surface energy effects in confined diblock copolymers, *Phys. Rev. Lett.* 76 (1996) 2503-2506.
- [199] V.F. Sears, Neutron scattering lengths and cross sections, *Neutron News* 3 (1992) 26-37.
- [200] C.K. Shelton, R.A.L. Jones, J.A. Dura, T.H. Epps, III, Pairing nanostructure reorganization during solvent vapor annealing with solvent-polymer preference in block polymer thin films via in situ neutron scattering, University of Delaware, 2016.
- [201] M.J. Park, N.P. Balsara, Phase behavior of symmetric sulfonated block copolymers, *Macromolecules* 41 (2008) 3678-3687.
- [202] S.Y. Kim, M.J. Park, N.P. Balsara, A. Jackson, Confinement effects on watery domains in hydrated block copolymer electrolyte membranes, *Macromolecules* 43 (2010) 8128-8135.
- [203] M.J. Park, K.H. Downing, A. Jackson, E.D. Gomez, A.M. Minor, D. Cookson, A.Z. Weber, N.P. Balsara, Increased water retention in polymer electrolyte membranes at elevated temperatures assisted by capillary condensation, *Nano Lett.* 7 (2007) 3547-3552.

- [204] M.D. Foster, M. Sikka, N. Singh, F.S. Bates, S.K. Satija, C.F. Majkrzak, Structure of symmetric polyolefin block copolymer thin films, *J. Chem. Phys.* 96 (1992) 8605-8615.
- [205] Q. Zhong, E. Metwalli, M. Rawolle, G. Kaune, A.M. Bivigou-Koumba, A. Laschewsky, C.M. Papadakis, R. Cubitt, J. Wang, P. Müller-Buschbaum, Influence of hydrophobic polystyrene blocks on the rehydration of polystyrene-block-poly(methoxy diethylene glycol acrylate)-block-polystyrene films investigated by in situ neutron reflectivity, *Macromolecules* 49 (2016) 317-326.
- [206] Q. Zhong, E. Metwalli, M. Rawolle, G. Kaune, A.M. Bivigou-Koumba, A. Laschewsky, C.M. Papadakis, R. Cubitt, P. Müller-Buschbaum, Structure and thermal response of thin thermoresponsive polystyrene-block-poly(methoxydiethylene glycol acrylate)-block-polystyrene films, *Macromolecules* 46 (2013) 4069-4080.
- [207] A. Modi, S.M. Bhaway, B.D. Vogt, J.F. Douglas, A. Al-Enizi, A. Elzatahry, A. Sharma, A. Karim, Direct immersion annealing of thin block copolymer films, *ACS Appl. Mater. Interfaces* 7 (2015) 21639-21645.
- [208] P. Muller-Buschbaum, Grazing incidence small-angle neutron scattering: challenges and possibilities, *Polym. J.* 45 (2013) 34-42.
- [209] W. Wang, E. Metwalli, J. Perlich, C.M. Papadakis, R. Cubitt, P. Müller-Buschbaum, Cyclic switching of water storage in thin block copolymer films containing poly(*n*-isopropylacrylamide), *Macromolecules* 42 (2009) 9041-9051.
- [210] W. Wang, E. Metwalli, J. Perlich, K. Troll, C.M. Papadakis, R. Cubitt, P. Müller-Buschbaum, Water storage in thin films maintaining the total film thickness as probed with in situ neutron reflectivity, *Macromol. Rapid Commun.* 30 (2009) 114-119.
- [211] P. Müller-Buschbaum, R. Cubitt, W. Petry, Nanostructured diblock copolymer films: A grazing incidence small-angle neutron scattering study, *Langmuir* 19 (2003) 7778-7782.
- [212] X. Zhang, B.C. Berry, K.G. Yager, S. Kim, R.L. Jones, S. Satija, D.L. Pickel, J.F. Douglas, A. Karim, Surface morphology diagram for cylinder-forming block copolymer thin films, *ACS Nano* 2 (2008) 2331-2341.
- [213] K.G. Yager, C. Forrey, G. Singh, S.K. Satija, K.A. Page, D.L. Patton, J.F. Douglas, R.L. Jones, A. Karim, Thermally-induced transition of lamellae orientation in block-copolymer films on 'neutral' nanoparticle-coated substrates, *Soft Matter* 11 (2015) 5154-5167.
- [214] M.M. Kulkarni, K.G. Yager, A. Sharma, A. Karim, Combinatorial block copolymer ordering on tunable rough substrates, *Macromolecules* 45 (2012) 4303-4314.

- [215] K.G. Yager, B.C. Berry, K. Page, D. Patton, A. Karim, E.J. Amis, Disordered nanoparticle interfaces for directed self-assembly, *Soft Matter* 5 (2009) 622-628.
- [216] X.H. Zhang, B.C. Berry, K.G. Yager, S. Kim, R.L. Jones, S. Satija, D.L. Pickel, J.F. Douglas, A. Karim, Surface morphology diagram for cylinder-forming block copolymer thin films, *ACS Nano* 2 (2008) 2331-2341.
- [217] G. Singh, K.G. Yager, D.-M. Smilgies, M.M. Kulkarni, D.G. Bucknall, A. Karim, Tuning molecular relaxation for vertical orientation in cylindrical block copolymer films via sharp dynamic zone annealing, *Macromolecules* 45 (2012) 7107-7117.
- [218] R.A. Register, Nanolithography: painting with block copolymers, *Nat. Nanotechnol.* 8 (2013) 618-619.
- [219] A.P. Marencic, R.A. Register, Controlling order in block copolymer thin films for nanopatterning applications, *Annu. Rev. Chem. Biomol. Eng.* 1 (2010) 277-297.
- [220] I.W. Hamley, Nanostructure fabrication using block copolymers, *Nanotechnology* 14 (2003) R39.
- [221] H.-C. Kim, S.-M. Park, W.D. Hinsberg, Block copolymer based nanostructures: materials, processes, and applications to electronics, *Chem. Rev.* 110 (2010) 146-177.
- [222] C. Park, J. Yoon, E.L. Thomas, Enabling nanotechnology with self assembled block copolymer patterns, *Polymer* 44 (2003) 6725-6760.
- [223] E. Gann, A.T. Young, B.A. Collins, H. Yan, J. Nasiatka, H.A. Padmore, H. Ade, A. Hexemer, C. Wang, Soft X-ray scattering facility at the advanced light source with real-time data processing and analysis, *Rev. Sci. Instrum.* 83 (2012) 045110.
- [224] I. Akiba, A. Takechi, M. Sakou, M. Handa, Y. Shinohara, Y. Amemiya, N. Yagi, K. Sakurai, Anomalous small-angle X-ray scattering study of structure of polymer micelles having bromines in hydrophobic core, *Macromolecules* 45 (2012) 6150-6157.
- [225] M. Sztucki, E. Di Cola, T. Narayanan, Anomalous small-angle X-ray scattering from charged soft matter, *Eur. Phys. J. Special Topics* 208 (2012) 319-331.
- [226] S.C. Vogel, A review of neutron scattering applications to nuclear materials, *ISRN Materials Science* 2013 (2013) 24.
- [227] R. Dimeo, R. Ibberson, S. O'Kelly, D. Neumann, R. Cappelletti, P. Gehring, The expansion of the nist center for neutron research, *Neutron News* 24 (2013) 29-31.

- [228] J.M. Simmons, J.C. Cook, R.M. Ibberson, C.F. Majkrzak, D.A. Neumann, Polychromatic energy-dispersive neutron diffraction at a continuous source, *J. Appl. Crystallogr.* 46 (2013) 1347-1352.
- [229] J.J. Rush, R.L. Cappelletti, The NIST center for neutron research: over 40 years serving NIST/NBS and the nation, National Institute of Standards and Technology, U.S. Government Printing Office, 2011.
- [230] M. Monkenbusch, D. Richter, High resolution neutron spectroscopy—a tool for the investigation of dynamics of polymers and soft matter, *C. R. Phys.* 8 (2007) 845-864.
- [231] R. Pynn, R. Ashkar, P. Stonaha, A.L. Washington, Some recent results using spin echo resolved grazing incidence scattering (SERGIS), *Physica B* 406 (2011) 2350-2353.
- [232] J. Major, A. Vorobiev, A. Rühm, R. Maier, M. Major, M. Mezger, M. Nülle, H. Dosch, G.P. Felcher, P. Falus, T. Keller, R. Pynn, A spin-echo resolved grazing incidence scattering setup for the neutron interrogation of buried nanostructures, *Rev. Sci. Instrum.* 80 (2009) 123903.
- [233] A.J. Parnell, R.M. Dalgliesh, R.A.L. Jones, A.D.F. Dunbar, A neutron spin echo resolved grazing incidence scattering study of crystallites in organic photovoltaic thin films, *Appl. Phys. Lett.* 102 (2013) 073111.
- [234] Y. Wataru, M. Atsushi, Grazing-incidence ultrasmall-angle X-ray scattering imaging with x-ray transmission gratings: a feasibility study, *Jpn. J. Appl. Phys.* 53 (2014) 05FH04.
- [235] F. Zhang, J. Ilavsky, Ultra-small-angle X-ray scattering of polymers, *Polym. Rev.* 50 (2010) 59-90.
- [236] D.W. Schaefer, M.M. Agamalian, Ultra-small-angle neutron scattering: a new tool for materials research, *Curr. Opin. Solid St. M.* 8 (2004) 39-47.
- [237] P. Klosowski, VSANS: very small angle neutron scattering. <https://www.ncnr.nist.gov/expansion/individual_instruments/vSANS053007.html>, 2012.
- [238] Y. Lu, H. Xia, G. Zhang, C. Wu, Electrically tunable block copolymer photonic crystals with a full color display, *J. Mater. Chem.* 19 (2009) 5952-5955.
- [239] Y. Fink, A.M. Urbas, M.G. Bawendi, J.D. Joannopoulos, E.L. Thomas, Block copolymers as photonic bandgap materials, *J. Lightwave Technol.* 17 (1999) 1963.
- [240] J. Yoon, W. Lee, E.L. Thomas, Self-assembly of block copolymers for photonic-bandgap materials, *MRS Bull.* 30 (2005) 721-726.

- [241] Y. Kang, J.J. Walish, T. Gorishnyy, E.L. Thomas, Broad-wavelength-range chemically tunable block-copolymer photonic gels, *Nat. Mater.* 6 (2007) 957-960.
- [242] M.B. Runge, N.B. Bowden, Synthesis of high molecular weight comb block copolymers and their assembly into ordered morphologies in the solid state, *J. Am. Chem. Soc.* 129 (2007) 10551-10560.
- [243] B. McCulloch, G. Portale, W. Bras, J.A. Pople, A. Hexemer, R.A. Segalman, Dynamics of magnetic alignment in rod-coil block copolymers, *Macromolecules* 46 (2013) 4462-4471.
- [244] X. Feng, M.E. Tousley, M.G. Cowan, B.R. Wiesenauer, S. Nejati, Y. Choo, R.D. Noble, M. Elimelech, D.L. Gin, C.O. Osuji, Scalable fabrication of polymer membranes with vertically aligned 1 nm pores by magnetic field directed self-assembly, *ACS Nano* 8 (2014) 11977-11986.
- [245] M. Gopinadhan, P.W. Majewski, Y. Choo, C.O. Osuji, Order-disorder transition and alignment dynamics of a block copolymer under high magnetic fields by in situ X-ray scattering, *Phys. Rev. Lett.* 110 (2013) 078301.
- [246] W. Yin, M. Dadmun, A new model for the morphology of P3HT/PCBM organic photovoltaics from small-angle neutron scattering: rivers and streams, *ACS Nano* 5 (2011) 4756-4768.
- [247] W.J. Durand, M.C. Carlson, M.J. Maher, G. Blachut, L.J. Santos, S. Tein, V. Ganesan, C.J. Ellison, C.G. Willson, Experimental and modeling study of domain orientation in confined block copolymer thin films, *Macromolecules* 49 (2016) 308-316.
- [248] E.W. Edwards, M.P. Stoykovich, M. Müller, H.H. Solak, J.J. de Pablo, P.F. Nealey, Mechanism and kinetics of ordering in diblock copolymer thin films on chemically nanopatterned substrates, *J. Polym. Sci., Part B: Polym. Phys.* 43 (2005) 3444-3459.
- [249] Y. Yin, P. Sun, R. Jiang, B. Li, T. Chen, Q. Jin, D. Ding, A.-C. Shi, Simulated annealing study of asymmetric diblock copolymer thin films, *J. Chem. Phys.* 124 (2006) 184708.
- [250] F.A. Detcheverry, G. Liu, P.F. Nealey, J.J. de Pablo, Interpolation in the directed assembly of block copolymers on nanopatterned substrates: simulation and experiments, *Macromolecules* 43 (2010) 3446-3454.
- [251] Z. Wang, B. Li, Q. Jin, D. Ding, A.-C. Shi, Simulated annealing study of self-assembly of symmetric a-b triblock copolymers confined in cylindrical nanopores, *Macromol. Theory Simul.* 17 (2008) 86-102.
- [252] A.F. Hannon, W. Bai, A. Alexander-Katz, C.A. Ross, Simulation methods for solvent vapor annealing of block copolymer thin films, *Soft Matter* 11 (2015) 3794-3805.

- [253] A.V. Berezkin, C.M. Papadakis, I.I. Potemkin, Vertical domain orientation in cylinder-forming diblock copolymer films upon solvent vapor annealing, *Macromolecules* 49 (2016) 415-424.
- [254] S.P. Paradiso, K.T. Delaney, C.J. García-Cervera, H.D. Cenicerós, G.H. Fredrickson, Block copolymer self assembly during rapid solvent evaporation: insights into cylinder growth and stability, *ACS Macro Lett.* 3 (2014) 16-20.
- [255] J.D. Cushen, L. Wan, G. Pandav, I. Mitra, G.E. Stein, V. Ganesan, R. Ruiz, C.G. Willson, C.J. Ellison, Ordering poly(trimethylsilyl styrene-block-(d),(l)-lactide) block copolymers in thin films by solvent annealing using a mixture of domain-selective solvents, *J. Polym. Sci., Part B: Polym. Phys.* 52 (2014) 36-45.
- [256] S.-M. Hur, G.S. Khaira, A. Ramírez-Hernández, M. Müller, P.F. Nealey, J.J. de Pablo, Simulation of defect reduction in block copolymer thin films by solvent annealing, *ACS Macro Lett.* 4 (2015) 11-15.
- [257] A. Stenbock-Fermor, A.A. Rudov, R.A. Gumerov, L.A. Tsarkova, A. Böker, M. Möller, I.I. Potemkin, Morphology-controlled kinetics of solvent uptake by block copolymer films in nonselective solvent vapors, *ACS Macro Lett.* 3 (2014) 803-807.
- [258] S.P. Paradiso, K.T. Delaney, C.J. García-Cervera, H.D. Cenicerós, G.H. Fredrickson, Cyclic solvent annealing improves feature orientation in block copolymer thin films, *Macromolecules* 49 (2016) 1743-1751.
- [259] D. Kan, X. He, Tuning phase structures of a symmetrical diblock copolymer with a patterned electric field, *Soft Matter* (2016).
- [260] T. Xu, A.V. Zvelindovsky, G.J.A. Sevink, O. Gang, B. Ocko, Y. Zhu, S.P. Gido, T.P. Russell, Electric field induced sphere-to-cylinder transition in diblock copolymer thin films, *Macromolecules* 37 (2004) 6980-6984.
- [261] A.V. Kyrilyuk, G.J.A. Sevink, A.V. Zvelindovsky, J.G.E.M. Fraaije, Simulations of electric field induced lamellar alignment in block copolymers in the presence of selective electrodes, *Macromol. Theory Simul.* 12 (2003) 508-511.
- [262] I.W. Hamley, Cell dynamics simulations of block copolymers, *Macromol. Theory Simul.* 9 (2000) 363-380.
- [263] L. Darré, J. Iglesias-Fernandez, A. Kohlmeyer, H. Wacklin, C. Domene, Molecular dynamics simulations and neutron reflectivity as an effective approach to characterize biological membranes and related macromolecular assemblies, *J. Chem. Theory Comput.* 11 (2015) 4875-4884.

[264] N. Kučerka, J. Katsaras, J.F. Nagle, Comparing membrane simulations to scattering experiments: introducing the simtoexp software, *J. Membr. Biol.* 235 (2010) 43-50.

AUTHORS BIOS

Cameron K. Shelton is currently pursuing his Ph.D. in Chemical and Biomolecular Engineering from the University of Delaware under the direction of Prof. Thomas H. Epps, III. He received his B.S. in Chemical Engineering and B.A. in Physics from the University of Virginia in 2012. His thesis work focuses on developing innovative approaches to characterize and direct the self-assembly of block copolymer thin film nanostructures.

Thomas H. Epps, III, is the Thomas and Kipp Gutshall Associate Professor of Chemical and Biomolecular Engineering and an Associate Professor of Materials Science and Engineering at the University of Delaware. He received a B.S. in Chemical Engineering (1998) from the Massachusetts Institute of Technology (MIT), an M.S. in Chemical Engineering (1999), and a Ph.D. in Chemical Engineering (2004) from the University of Minnesota under the direction of Prof. Frank S. Bates. He has received several awards including the John H. Dillon Medal from APS, Owens-Corning Award from AIChE, Sigma Xi Young Investigator Award, DuPont Young Professor Award, Department of Defense PECASE Award, Air Force Young Investigator Award, and NSF Career Award among others. His research focuses on the design, synthesis, and characterization of nanostructured soft materials and bio-based systems in bulk, thin film, and

solution environments for lithographic templating, separation membrane, ion-transport, thermoplastic elastomer, and drug delivery applications.

GRAPHICAL ABSTRACT