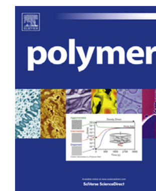
Polymer 105 (2016) 545–561

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Block copolymer thin films: Characterizing nanostructure evolution with *in situ* X-ray and neutron scattering

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A R T I C L E I N F O

Article history:
Received 21 May 2016
Accepted 28 June 2016
Available online 7 July 2016

Keywords:
Block copolymer thin film
Annealing
Nanostructure reorganization
In situ characterization
X-ray scattering
Neutron scattering

A B S T R A C T

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-assembly into nanoscale features. To direct the self-assembly of BCP thin film nanostructures, a suite of annealing techniques has 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.

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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) [1–9]. 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 [10–15]. Additionally, thin film deposition methods (*e.g.*, spin-casting, flow coating, dip coating, zone-casting, electrospray) can greatly affect the as-cast morphology [12,16–19]. To guide phase separation for a given application, BCP thin films often are subjected to various post-processing techniques designed to modulate specific interactions [11–13,20]. Common avenues include thermal annealing [21,22], solvent vapor annealing (SVA) [23–25], solvothermal annealing [26–28], microwave-assisted SVA [29,30], chemical substrate modification and patterning [31–35], graphoepitaxy [36–39], electrical/magnetic field alignment [40–44], and shear alignment [45–51], each of which has its own set of advantages and disadvantages [3,13,20,52,53]. 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

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http://dx.doi.org/10.1016/j.polymer.2016.06.069
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to understand the inherent mechanisms behind each annealing technique to achieve cost-effective and scalable control over the morphological evolution [54]. 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, electric/magnetic 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 [44,55–57]. 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 [34,58,59]. Additionally, *in situ* atomic force microscopy (AFM) has been used to examine nanoscale restructuring during thermal annealing [60–67], electrical field alignment [68], and SVA [69–73]. 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 [74–80]. Data from these SE/SR measurements have been analyzed to calculate polymer-solvent interaction parameters [69,81], construct surface structure phase diagrams [25,82], and understand thickness dependent self-assembly mechanisms [41,79,83,84]. 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 [85,86]. 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 [13,52,53,87–91]. 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 Fig. 1) [88,92,93]. 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.

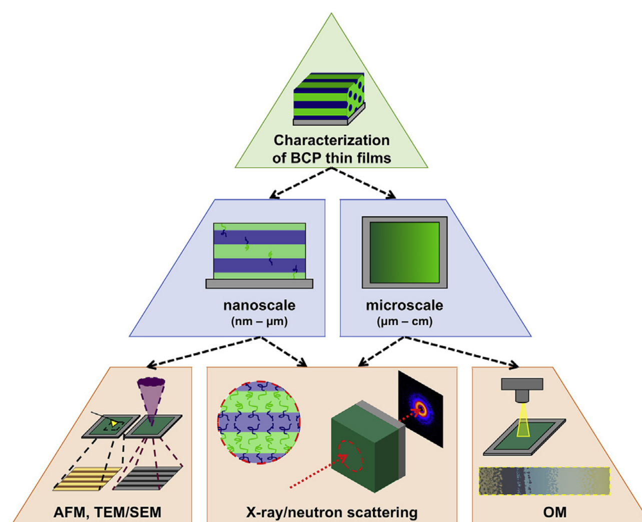

Fig. 1. Common characterization techniques used to analyze BCP thin film self-assembly. Many techniques, such as AFM, TEM, and SEM, only probe nanoscale areas and features, and others, such as OM, only probe microscale areas and features. X-ray and neutron scattering techniques allow interrogation of 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 [53,94,95]. 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) [96]. 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 [96]. For a detailed explanation of X-ray scattering, the reader is directed to the literature [88,97,98]. Key advantages of X-ray scattering for *in situ*

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