



Deciphering the three-dimensional morphology of free-standing block copolymer thin films by transmission electron microscopy

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ABSTRACT

Block copolymer thin films with distinct morphologies are prepared by spin casting a nominally lamellar assay of poly(styrene-block-ethylene oxide) from a variety of solvents with and without salt doping. The 3-D morphologies of free-standing thin-film regions, which are obtained by casting directly onto holey substrates, are investigated in detail using various energy-filtering transmission electron microscopy techniques and by electron tomography. Surface characterization is achieved by atomic force microscopy. Our results demonstrate that in order to fully characterize the unique 3-D morphologies of the block copolymer thin films, a multi-method approach is required. When casting from a binary solvent, an unexpected layered honeycomb-type morphology is revealed, which likely results from an expansion of the poly(ethylene oxide) phase. A dramatic effect of selective cation coordination on the morphology of the as-cast block copolymer films is also directly observed.

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1. Introduction

The self-assembly of block copolymers into ordered nanostructures is an area of intense research in which thin-film geometries feature widely. Applications of block copolymer thin films include porous membranes for the filtration of biomolecules (Yang et al., 2010), flexible membranes for organic photovoltaics and light-emitting devices (Segalman et al., 2009), and electrolyte membranes for batteries and fuel cells (Orilall and Wiesner, 2011). Targeted selection of the constituent blocks of the copolymer enables the synthesis of new materials with unique properties. Coupled with the rich array of morphologies forming upon phase separation, seemingly inexhaustible technological possibilities result (Bates and Fredrickson, 1999). Since the desired behavior of the block copolymer is intimately linked to its morphology, a deep understanding of the structures forming upon phase separation is required. Consequently, effective techniques for the structural characterization of block copolymers are of crucial importance.

Block copolymer phase separation is driven by competing enthalpic and entropic effects, which must be balanced in order for thermodynamic equilibrium to be reached. Since the blocks of the copolymer molecule are joined by a covalent bond, phase separation proceeds on nanometer levels (Bates and Fredrickson, 1990; Bates, 1991). The particular morphology formed in the bulk material is determined by the relative volume fractions of the polymer blocks and by the segregation strength between them, quantified by the Flory–Huggins interaction parameter. In the bulk, self-assembly generally manifests as grains of ordered domains arranged randomly throughout the material. In contrast, in thin films interfacial energy effects result in ordering over much longer length scales and can be used to control domain orientations (Marencic and Register, 2010; Fasolka and Mayes, 2001; Albert and Epps, 2010).

The domain spacings of the block copolymer can range from several hundred to just a few nanometers in size, hence techniques for the structural characterization of these materials must also be sensitive at the nanoscale. Investigations based on X-ray and neutron scattering effects are routinely implemented, as are several direct imaging techniques. Direct imaging of sectioned bulk specimens and thin films can be achieved by transmission electron microscopy (TEM), with recent advances in instrumentation having resulted in a surge in the use of energy-filtering methods for imaging this class of soft matter (Libera and Egerton, 2010).

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Energy-filtering enables the generation of image contrast without the need for heavy-element stains, which are often of low selectivity and are known to produce artifacts. For the direct imaging of block copolymer surfaces, atomic force microscopy (AFM) and scanning electron microscopy (SEM) are further invaluable tools.

In this study, poly(styrene-block-ethylene oxide) (PS-*b*-PEO) thin films (<200 nm in thickness) with distinct morphologies are prepared by spin casting from various solvents with and without salt doping. PS-*b*-PEO is a favorable candidate for the dry polymer electrolyte in solid-state rechargeable lithium-ion batteries, since it combines a soft phase for ion conduction (PEO) with a hard phase for mechanical strength (PS) (Singh et al., 2007). In current lithium polymer batteries the polymer electrolyte membrane is around 15 μm in thickness, yet in order to probe the limits of microbattery fabrication, investigations of much thinner films are also important. The lithium ions in the block copolymer are coordinated by the ether groups of the PEO block and ion transport is mediated by segmental motion of the PEO chains (Druger et al., 1983). It is observed that the phase behavior of the block copolymer is strongly influenced by salt concentration, resulting from a combination of effects including suppression of crystallinity in the PEO phase and modification of the Flory–Huggins interaction parameter due to selective cation co-ordination (Epps et al., 2002, 2003; Young and Epps, 2009; Metwalli et al., 2011). Various effects of block copolymer morphology on the ion transport properties of the electrolyte have also emerged (Singh et al., 2007; Mullin et al., 2011).

The morphologies of the various PS-*b*-PEO films prepared here are characterized in detail by TEM. By casting directly onto holey substrates, stable free-standing thin regions ideal for TEM analysis are obtained. This relatively straightforward sample preparation process avoids the need for more challenging preparation techniques such as the transfer of fragile thin films from continuous substrates, or embedding of thin films in resin and subsequent sectioning to obtain electron-transparent segments (Radzilowski et al., 1996). It should be noted, however, that the morphologies of the free-standing films can differ from those of their substrate-supported counterparts due to interfacial energy effects (Fasolka and Mayes, 2001). We make extensive use of energy-filtering TEM (EFTEM) to obtain high-contrast elastic images, thickness maps, and chemical maps (Libera and Egerton, 2010; Egerton, 2011; Du Chesne, 1999) of the free-standing thin-film specimens. In addition, tilt series of energy-filtered elastic images are acquired for tomographic reconstructions (Midgley and Weyland, 2003; Jinnae and Spontak, 2009). The results obtained using the various TEM techniques described are then combined to precisely determine the 3-D morphologies of the PS-*b*-PEO films. To augment the TEM results, surface characterization of the thin films is performed by atomic force microscopy (AFM).

2. Experimental

2.1. Thin-film preparation

The films were prepared using a PS-*b*-PEO diblock copolymer with number molecular weights for the PS and PEO blocks of 74 and 98 kg/mol, respectively, and a polydispersity index of 1.14. The polymer was synthesized via anionic polymerization and forms a lamellar morphology in the bulk with a domain spacing of 100 nm (Singh et al., 2007). Polymer electrolyte solutions for spin casting were prepared using acetonitrile, N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and benzene solvents. The salts used were lithium/sodium hexafluorophosphate (PF_6^-) and trifluoromethanesulfonate (Tf^-), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Acetonitrile is a selective solvent for PS-*b*-PEO, solvating only the PEO block. In contrast, NMP, THF and benzene are good

solvents for both blocks. The ionic salts are solvated by the polar solvents acetonitrile, NMP and THF, although the relative solubilities vary.

For the purposes of this study, thin films were cast from (1) acetonitrile, (2) NMP, and (3) benzene-THF. The salts and PS-*b*-PEO were dried before use, and all samples were prepared in an argon glovebox. For the acetonitrile and NMP solutions, a given salt was first dissolved in the solvent and PS-*b*-PEO then added to achieve a polymer concentration in the solution of 1% by weight. Salt concentrations, r , of 1/60, 1/12, and 1/6 cations per ethylene oxide moiety were targeted. For the binary benzene-THF combination, separate solutions consisting of 10% by weight salt in THF and 1% by weight PS-*b*-PEO in benzene were first prepared. Then a few drops of the salt-THF solution were added to the PS-*b*-PEO in benzene to give a salt concentration r of 1/12. The resulting ratio of benzene to THF was 97 to 3% by weight. Solutions of PS-*b*-PEO in the absence of salt were also prepared using each of the three solvent systems discussed. In the case of the binary solvent combination, the same ratio of benzene to THF was used as before.

Free-standing thin films were obtained by spin casting onto holey silicon nitride TEM substrates purchased from Ted Pella. Each substrate was mounted onto a metal disc, using small tabs of removable tape, in order to enable placement onto the vacuum chuck of the spin coater. For each sample, 5 μL of polymer solution were pipetted onto the substrate, which was then spun at 2800 rpm for 60 s. All TEM samples were left to dry in the glovebox for at least 24 h and were then transported in a desiccator.

2.2. Thin-film characterization

Characterization of the free-standing, unstained films by TEM was performed at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory (LBNL), using a Zeiss Libra 200MC operated at 200 kV and the TEAM 0.5 microscope operated at 80 kV, and at the Molecular Foundry, LBNL, using a Zeiss Libra 120 PLUS operated at 120 kV. These electron microscopes are equipped with energy filters enabling various EFTEM-based mapping techniques and the implementation of zero-loss filtering to improve contrast in bright-field images by reducing the image blurring caused by chromatic aberrations and inelastically scattered electrons.

Local thickness variations in the thin films were investigated by recording zero-loss filtered and unfiltered images of the same region and applying the standard log-ratio method to generate a relative thickness map (Egerton, 2011). Chemical mapping was performed by implementing EFTEM spectrum-imaging of the plasmon resonance in the low electron energy-loss range, which serves as a chemical fingerprint for different polymer types. The EFTEM spectrum-image datasets were typically implemented using a slit width of 5 eV to record a series of filtered images across the energy-loss range of 5–60 eV in 1 eV steps. The acquisition time for each image was 0.5 s and the dose rate was of the order of $10^5 \text{ e}^-/\text{nm}^2/\text{s}$. By applying principal component analysis to the low-loss spectrum-image datasets, as described in a previous work (Allen et al., 2011), even subtle differences in the plasmon peak shapes can be detected and hence used to distinguish chemical phases.

Tilt series of zero-loss filtered images for tomographic reconstructions were recorded manually at the 200MC Zeiss Libra. In a typical series, images were recorded with an acquisition time of 0.5 s from -60 to $+60^\circ$ in 2° intervals. The dose rate was $\sim 10^5 \text{ e}^-/\text{nm}^2/\text{s}$. Compensations for sample drift and image focus were implemented between successive image acquisitions as required. Three-dimensional reconstructions were then obtained from the tilt series by applying an algorithm for weighted back-projection (Midgley and Weyland, 2003). Given the electron dose

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