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Thomas M. Bennett
Kevin Pei
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Thomas M. Bennett, a,b Kevin Pei, a Han-Hao Cheng, a Kristofer J. Thurecht, a,b,d Kevin S. Jack, e and Idriss Blakey, a,b,*

aUniversity of Queensland, Australian Institute for Bioengineering and Nanotechnology, Brisbane, Queensland 4072, Australia
bCentre for Advanced Imaging, Brisbane, Queensland 4072, Australia
cAustralian National Fabrication Facility, QLD Node, Brisbane, Queensland 4072, Australia
dARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Brisbane, Queensland 4072, Australia
eCentre for Microscopy and Microanalysis, Brisbane, Queensland 4072, Australia

Abstract. Directed self-assembly (DSA) is a promising approach for extending conventional lithographic techniques by being able to print features with critical dimensions under 10 nm. The most widely studied block copolymer system is polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA). This system is well understood in terms of its synthesis, properties, and performance in DSA. However, PS-b-PMMA also has a number of limitations that impact on its performance and hence scope of application. The primary limitation is the low Flory-Huggins polymer-polymer interaction parameter (χ), which limits the size of features that can be printed. Another issue with block copolymers in general is that specific molecular weights need to be synthesized to achieve desired morphologies and feature sizes. Here we explore blending ionic liquid (IL) additives with PS-b-PMMA to increase the χ parameter. ILs have a number of useful properties that include negligible vapor pressure, tunable solvent strength, thermal stability, and chemical stability. The blends of PS-b-PMMA with an IL selective for the PMMA block allowed the resolution of the block copolymer to be improved. Depending on the amount of additive, it is also possible to tune the domain size and the morphology of the systems. These findings may expand the scope of PS-b-PMMA for DSA. © 2014 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JMM.13.3.031304]

Keywords: Ionic liquids; block copolymer; PS-b-PMMA; χ parameter; Flory-Huggins polymer-polymer interaction parameter.

1 Introduction

Directed self-assembly (DSA) is an approach that combines photolithography (top-down) and self-assembly of block copolymers (bottom-up) to achieve ordered features with sub-lithographic resolution.1,12 Block copolymers are made up of at least two chemically distinct polymer chains that are covalently linked. When the respective blocks are incompatible, arrays of highly ordered nanostructures can form. The equilibrium morphology depends on the relative volume fraction (f) of each block, the degree of polymerization (N) and degree of incompatibility, i.e., the Flory-Huggins polymer-polymer interaction parameter (χ).13 There are two main approaches for carrying out DSA, namely chemoepitaxy and grahopoitaxy. Chemoepitaxy relies on chemically patterning a substrate, where typically one of the components of the pattern preferentially interacts with one of the blocks and subsequently drives the ordering during self-assembly.14,15 On the other hand, grahopoitaxy uses surface topography, e.g., a printed resist, to guide self-assembly and align the phase-separated domains.16–20

Polystyrene-block-poly(methyl methacrylate), or PS-b-PMMA, is currently the most widely studied system, where DSA of PS lines with a pitch of ~24 nm has been demonstrated.21 There is also a significant body of knowledge relating to optimization of processing and integration with manufacturing processes.22–25 Nonetheless, PS-b-PMMA has some limitations in its scalability and compatibility for future nodes of fabrication because (a) it has a small Flory-Huggins polymer-polymer interaction parameter (χPS-PMMA = 0.04 at room temperature),26 limiting the ultimate resolution, and (b) annealing temperatures that are reported are significantly higher than the glass temperature (Tg) of typical positive tone photoresists. As a result, next-generation materials that can achieve better resolutions are being actively studied. Recently, we have reported our investigations of a high-χ BCP, polystyrene-b-poly(DL-lactide) (PS-b-PLA), which overcomes some of these issues. Zalusky et al. have shown that χPS-PLA was equal to 0.217 at room temperature, enabling much smaller domain sizes. Our initial efforts involved identifying the interfacial interactions of PS-b-PLA with substrates that were modified with a series of crosslinked matrices of statistical copolymers of PS and PMMA. Lamellae oriented perpendicular to the substrate with domain sizes as small as 8 nm could be achieved. Graphopoitaxy-based DSA was also carried out with this system, where no resist freezing step was required when using a polyhydroxystyrene-based photoresist template. This was because the spin-coating solvent for the BCP was a nonsolvent for the photoresist and the annealing temperature required to induce order was below the Tg of the photoresist.29 While this system was promising, to achieve feature sizes smaller...
than 8 nm would require the development of systems with even higher $\chi$ parameters. While there are a number of candidates that have been reported,30–33 the disadvantage of such systems is that the development cycle can be prohibitively long. For example, neutral surfaces may need to be identified and annealing conditions developed.

Another option for increasing $\chi$ utilizes solvent vapor annealing, where solvent vapor is used to swell one or both blocks in a BCP and under the correct conditions can tune domain sizes and transition a system from one morphology to another.34–38 These morphological changes can then be kinetically trapped by flash removal of the solvent from the system. However, a disadvantage of this approach is that this additional step requires additional infrastructure in the fab (semiconductor fabrication facility) and strict control over the experimental parameters to achieve reproducible results.

The aim of this paper is to demonstrate that simple addition of additives to PS-$b$-PMMA [Fig. 1(a)] can be used to tune structural parameters such as morphology and pitch. Ionic liquids (ILs) were the initial class of additives chosen. ILs are low-melting-point salts which generally consist of a large organic cation with low symmetry that is paired with an inorganic or organic polyatomic anion that is usually weakly basic and possesses a diffuse, or protected charge.39 ILs are defined as salts with a melting point below 100°C, but the majority of ILs are liquid at or below room temperature.40 The completely ionic composition of ILs endows them with a range of properties, which makes them attractive candidates for both the replacement of many traditional organic solvents and as useful materials in a variety of applications. These properties include nonflammability, high chemical and thermal stability, high conductivity, negligible vapor pressure, and relatively low toxicity compared to many other common organic solvents.31,42 In terms of use as an additive for BCP formulations, the negligible vapor pressure, tunable solvent strength, chemical stability, and thermal stability make ILs an attractive option.

Many of the initial reports of BCP-IL mixtures focused on relatively dilute solutions of BCPs in ILs, where the morphology of micellar structures was studied.43–45 More recently, there have been reports on more concentrated systems where it has been demonstrated that blending ILs with BCPs such as PS-$b$-poly(2-vinyl pyridine),46–48 PS-$b$-poly(ethylene oxide)49 [PEO], and PEO-$b$-poly(propylene oxide)-$b$-PEO50 can lead to changes in morphology and $d$-spacing of the phase-separated domains. In this study, we blend 1-ethyl-3-methylimidazolium [emim] bis(trifluoromethanesulfonyle)amide [NTf$_2$] [Fig. 1(b)] with PS-$b$-PMMA and investigate the following questions: (i) Can the effective $\chi_{PS,PMMA}$ be increased? (ii) Can the long period/pitch be tuned? and (iii) Can the morphology of a system be switched? These questions are represented schematically in Fig. 2, which shows how addition of ILs might help to traverse the BCP phase diagram.

2 Experimental Methods
2.1 Polymer Materials and Characterization
PS-$b$-PMMA block copolymers were purchased from Polymer Source Inc. and used without further purification. The dispersity of each block copolymer was assessed by GPC and found to be $\leq$1.18. The PS-$b$-PMMA block copolymers are designated PS-$b$-PMMA (X-Y), where X and Y denote the number averaged molecular weights ($M_a$) in Da of the PS and PMMA blocks, respectively. The total $M_a$, dispersity (D), volume fraction of polystyrene ($f_{PS}$), and degree of polymerization (N) are given in Table 1.

![Fig. 1](image-url) (a) Structure of PS-$b$-PMMA. (b) Structure of the cation (top) and anion (bottom) of the ionic liquid (IL).

![Fig. 2](image-url) A schematic of a representative phase diagram for a diblock copolymer such as PS-$b$-PMMA, showing how the morphology of the block copolymer varies with volume fraction of PS ($f_{PS}$) and the degree of polymerization (N). The block arrows show the anticipated trajectories of the system when ILs that are selective for the PMMA block are introduced, where i) is transitioning from disordered to a lamellar morphology, ii) is tuning the pitch of lamellae, and iii) is transitioning from a cylindrical to lamellar morphology.
2.3 Vacuum in a desiccator to avoid water absorption.

The surface of each silicon wafer was finally in deionized water for 3 min, followed by drying in an oven for 10 min at 100°C. The silicon wafers used in this study were initially cleaned by sonication in methanol for 3 min, acetone for 3 min, and a gas flow rate of 10 sccm, a chamber pressure of 50 mTorr, a power of 150 W, and an exposure time of 60 s. Following the cleaning processes, all wafers were stored in a class 100 clean room prior to use.

2.4 Preparation of PS-r-PMMA Underlayers on Silicon Wafers

Statistical copolymers of polystyrene, poly(methyl methacrylate), and poly(glycidyl methacrylate) (PS-stat-PMMA-stat-PGMA) were prepared, as reported by Keen et al.28 The statistical copolymers (0.5 wt/v%) were dissolved in propylene glycol monomethyl ether acetate (PGMEA), along with triphenylsulfonium triflate (5 wt% with respect to the polymer). The solutions were spin coated at 4000 rpm onto silicon wafers. The coated substrates were annealed on a hot plate at 120°C for 60 s and then flood exposed with UV radiation (wavelength = 320–390 nm, dose = 180 mJ/cm²), followed by further annealing on a hot plate at 150°C for 300 s. All films had thicknesses between 10 and 20 nm as determined by ellipsometry. The characteristics of the five statistical copolymers used to produce the underlayers are detailed in Table 2. All copolymers contained 5 mol % PGMA.

2.5 Preparation of PS-b-PMMA/emim NTf₂ Bulk and Thin Films

Thin films of PS-b-PMMA/emim NTf₂ were spin coated from PGMEA solutions onto a series of wafers coated with different underlayers. The desired thickness of the films studied was either 0.5 or 1 long periods, L₀, of the block copolymer being used, which was achieved by modifying the concentration of the block copolymer solutions and by adjusting the spin speed of the spin coater. Bulk films were prepared by solution casting onto Kapton films. Samples were annealed at 220°C on a hotplate for 300 s and specified for a further 16 h at 200°C under a nitrogen atmosphere.

2.6 Morphology Characterization of Bulk Films via Small-Angle X-ray Scattering

The bulk morphology of the block copolymer/IL blends were determined using small-angle x-ray scattering (SAXS) on the Australian Synchrotron SAXS/WAXS beamline. The beamlne was configured with an x-ray wavelength of λ = 1.512 Å (8.2 keV) and focused to a 235 μm horizontal x 140 μm vertical spot. Two dimensional (2-D) scattering patterns were recorded on a Dectris-Pilatus 1M detector with an active area of 169 x 179 mm and a sample to detector distance of 3,412 m. The scattering patterns were then radially integrated to give one-dimensional (1-D) scattering profile as intensity (I) versus wave vector \( q = 4\pi \sin(\theta/2)/\lambda \), where \( \theta \) is the scattering angle and \( \lambda \) is the x-ray wavelength. Each scattering profile was also corrected for the empty cell scattering (Kapton film) using scatter Brain Analysis version 1.73 before morphological assignment.

2.7 Differential Scanning Calorimetry

A 1 STAR® DSC system (Mettler Toledo, Greifensee, Switzerland) was used to determine the glass transition temperatures of each block copolymer/IL mixture. Approximately 10 mg of each mixture was dissolved into DCM at a concentration of 10 wt. % and solution cast into aluminum DSC crucibles.

The samples were heated at 50°C for 18 h overnight in a vacuum oven to remove remaining solvent and then annealed at 200°C for 24 h under a nitrogen atmosphere. Upon cooling to room temperature, each crucible was sealed by crimping an aluminum lid on top. Indium and zinc were used as calibration standards for the DSC. Samples underwent two heating and cooling cycles from 30°C to 200°C, and the glass transitions were measured from the second heating cycle. The DSC employed a heating rate of 10°C/min and a N₂ flow rate of 15 ml/ min. All results were processed and analyzed using DSC 1 STAR® software version 9.10.

2.8 Morphology Characterization of Thin Films by Grazing-Incidence SAXS

Grazing-incidence small-angle x-ray scattering (GISAXS) measurements of selected thin films of the BCP/IL blends were acquired on the Australian Synchrotron SAXS/WAXS beamline. The beamline was configured as described in the section on SAXS above with the exception that the x-ray

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**Table 1** Block copolymer characteristics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total ( M_n ) (kDa)</th>
<th>( D )</th>
<th>( f_{PS} )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-b-PMMA (10k-b-10k)</td>
<td>20</td>
<td>1.18</td>
<td>0.53</td>
<td>196</td>
</tr>
<tr>
<td>PS-b-PMMA (38k-37k)</td>
<td>74.8</td>
<td>1.08</td>
<td>0.54</td>
<td>732</td>
</tr>
<tr>
<td>PS-b-PMMA (96k-36k)</td>
<td>132</td>
<td>1.11</td>
<td>0.75</td>
<td>1281</td>
</tr>
</tbody>
</table>

**Table 2** Underlayer characteristics.

<table>
<thead>
<tr>
<th>Underlayer</th>
<th>Total ( M_n ) (kDa)</th>
<th>( D )</th>
<th>Mole (%) PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>23</td>
<td>1.26</td>
<td>75</td>
</tr>
<tr>
<td>U2</td>
<td>50</td>
<td>1.41</td>
<td>69</td>
</tr>
<tr>
<td>U3</td>
<td>30</td>
<td>1.29</td>
<td>65</td>
</tr>
<tr>
<td>U4</td>
<td>46</td>
<td>1.41</td>
<td>62</td>
</tr>
<tr>
<td>U5</td>
<td>62</td>
<td>1.58</td>
<td>52</td>
</tr>
</tbody>
</table>
beam was focused to a 235 μm horizontal × 140 μm vertical spot and was impinged on the surface of the film at an incidence angle of 0.05 deg. The 2-D scattering patterns were then integrated in horizontal sectors along the \( q_{xy} \) plane to give 1-D scattering profiles.

### 2.9 Scanning Electron Microscopy

The morphologies of selected films were analyzed using a JEOL JSM-7800F scanning electron microscope (SEM). Films were mounted onto appropriate stubs using carbon tape and stored in a vacuum oven at 50°C for 16 h prior to analysis. In a typical setup, SEM micrographs were collected using an in-lens secondary electron detector with a working distance of 2.7 mm while operating a 1-kV gentle beam with a stage bias of 2 kV.

### 2.10 Atomic Force Microscopy

A MFP-3D (Asylum Research) atomic force microscope was used for all the measurements. The cantilevers used were HA_NC (Etalon) from NT-MDT, Russia, having a nominal resonant frequency of 140 kHz. All the images were obtained by employing tapping mode of the atomic force microscopy (AFM) in air. The AFM is mounted on an antivibration table (Herzan) and operated within an acoustic isolation enclosure (TMC, USA). The scan speed employed for each film was 1 Hz, and the data presented here are phase images of the films.

### 3 Results and Discussion

#### 3.1 Investigation of the Effect of Blended emim NTf\(_2\) on the Bulk Morphology of PS-\(b\)-PMMA

The bulk phase morphology of blends of PS-\(b\)-PMMA with varying amounts of the emim NTf\(_2\) was studied using transmission SAXS. The SAXS profiles provide information on the morphology present by interpretation of the relative spacings of the diffraction peaks and the interdomain distances from their absolute positions in \( q \) space.

#### 3.1.1 Inducing order in a system that is normally disordered in the bulk phase

Figure 3(a) shows the SAXS profiles (intensity versus \( q \)) of PS-\(b\)-PMMA (10k-\(b\)-10k) blended with 0% and 5% of emim NTf\(_2\). The sample with 0% emim NTf\(_2\) exhibited a single broad peak, which was indicative of a disordered morphology. This result was predicted for this system, because \( \chi_N \) was \( \sim 8 \) at room temperature, which is below the minimum value of 10.5 that is predicted by mean field theory to achieve a lamellar phase.\(_{13} \)
On the other hand, the sample with 5% emim NTf2 had a SAXS profile that was characteristic of a lamellar morphology, having Bragg peaks at 2 and 3 times q*. This indicated that for this particular formulation, the IL increased the effective ξPS-PMMA parameter by at least 31%, i.e., such that the effective ξN was greater than 10.5. This was attributed to emim NTf2 being a good solvent for PMMA chains and a poor solvent for the PS. Hence, upon forming a block copolymer/IL blend, the emim NTf2 preferentially interacts with the PMMA chains and screens the PMMA/PS interactions. This has the effect of decreasing the compatibility of the PMMA and PS chains, which increases the effective ξPS-PMMA parameter.

An advantage of blends of block copolymers with ILs is that, because of their negligible vapor pressures, the ILs will not evaporate under typical processing conditions used in DSA, so they do not require specialized vapor annealing chambers, and precise amounts of the IL can be added during preparation of the BCP solutions. For example, the blends of PS-b-PMMA and emim NTf2 could be annealed to 220°C, and the SAXS profile measured at that temperature remained unchanged. This indicated that the morphology remained unchanged over temperatures spanning from 23°C to 220°C. Perhaps the most distinct advantage of this approach is that it provides access to size scales below the 24-nm pitch resolution limit of neat PS-b-PMMA. For example, the long period (pitch) of the PS-b-PMMA (10k-b-10k) with 5% emim NTf2 was 20 nm. Further studies on systems with smaller block lengths are currently ongoing in our labs to assess the potential of this approach to improve resolution beyond 20 nm.

### 3.1.2 Tuning the domain spacing of lamellae by increasing the IL content

Figure 3(b) shows a series of SAXS profiles, focusing on q*, for PS-b-PMMA (38k-b-37k) blended with emim NTf2 at concentrations varying from 0% to 12%. It can be seen that q* shifts to smaller values with increasing emim NTf2 content. This indicates that the lamellar spacing increased as a function of emim NTf2 content. This is quantified in Fig. 3(c), which shows that the long period of the lamellar morphology was ∼39 nm for the neat BCP and this could be tuned up to 50.6 nm, an increase of almost 30%, by blending up to 12% emim NTf2. In this case, the long period could be incremented by about 0.9 nm per percent of emim NTf2 in the system. This change in spacing could be attributed to preferential swelling of the PMMA domain with increasing amounts of emim NTf2. Importantly for DSA applications, this demonstrates that the pitch of a given BCP can be tuned to a desired size by simply incorporating a specific volume fraction of emim NTf2 into the formulation. For example, a specific advantage may be that a BCP of a given molecular weight could be tuned such that it can be used for a wider range of pitches, perhaps reducing the need for extensive libraries of BCPs to cater to different pitch requirements.

### 3.1.3 Tuning the morphology of block copolymers by blending emim NTf2

Figure 3(d) shows the SAXS profiles of PS-b-PMMA (38k-b-37k) with 0% and 17% emim NTf2. The sample with no emim NTf2 exhibits the characteristic profile for a lamellar morphology, whereas the sample with 17% emim NTf2 exhibits a hexagonal (cylindrical) morphology. This demonstrates that the material could transition between morphologies when a sufficient volume fraction of emim NTf2 was added. Again, this concept may also be useful for DSA in that it broadens the scope of application of a particular block copolymer sample.

### 3.1.4 Other factors that may influence applicability to DSA

The effect of the additives on the etch selectivity of the blocks is an important factor to consider for the applicability using blends of ILs and BCPs for DSA. While etch resistance studies are beyond the scope of this article, it might be anticipated that the high fluorine content would impart the IL with a lower etch resistance than PMMA. Hence, incorporation of IL into the PMMA block may decrease the etch resistance and consequently increase the etch selectivity between the PS and PMMA blocks.

The second factor that is important to consider is how the IL impacts on the glass transition temperature of the block copolymer. The DSC thermograms for blends of PS-b-PMMA (38k-b-37k) with emim NTf2 at polymer fractions of 1.00, 0.90, 0.75, and 0.60 are shown in Fig. 4. The neat PS-b-PMMA (38k-b-37k) exhibits two glass transition temperatures. The first is at 107°C (assigned to PS) and the second at 132°C (assigned to PMMA). Upon incorporation of 10% emim NTf2, only a single Tg at 106°C could be observed, and this decreased slightly to 104°C for IL concentrations of 25% and 40%. Based on the solubility of PMMA in emim NTf2 and insolubility of PS in IL, these results were attributed to the PMMA block being plasticized, and the PS block remaining essentially unaffected. In support of this, Susan et al. have shown that blends of PMMA homopolymer and emim NTf2 have Tg values below room temperature for similar degrees of incorporation. The fact that the PS Tg remains virtually unchanged is a positive for its application in DSA, because the PS domains are the domains that will remain after reactive ion etching due to their higher etch resistance.

![Fig. 4 DSC thermograms for blends of PS-b-PMMA (38k-b-37k) with emim NTf2 for polymer fractions of 1.00, 0.90, 0.75, and 0.60.](image-url)
3.2 Investigation of the Effect of Blended \(\text{emim NTf}_2\) on the Thin Film Morphology and Interfacial Properties of PS-b-PMMA

3.2.1 Identifying a neutral surface

It is well known that the balance of interactions between each block and the substrate of air interface can have a significant effect on the orientation of domains in block copolymer thin films. For example, if the substrate preferentially interacts with one of the blocks, then for a BCP that has a lamellar morphology, the domains can orient parallel to the substrate.56 On the other hand, if the substrate has non-preferential interactions with both blocks, then the domains orient perpendicular to the substrate.57

When blending an additive, such as an IL, into the BCP is that the surface energetics may change drastically, necessitating the identification of new compositions for "neutral" underlayers.

To determine whether blending of \(\text{emim NTf}_2\) had an effect on the interaction with the underlay, Solutions of PS-b-PMMA (38k-b-37k) blended with 20\% IL in PGMEA were spin coated onto underlayers composed of statistical copolymers of PS and PMMA that had PS compositions ranging from 52\% to 75\%. From our previous studies for this particular type of underlayer, this range encompassed the neutral window for PS-b-PMMA.12 Figure 5 shows low-resolution (20 \(\times\) 20 \(\mu\text{m}\) field-of-view) AFM images for three underlayers, (a) 69\% PS, (b) 65\% PS, and (c) 62\% PS. When the underlayer with 69\% PS was used [Fig. 5(a)], dewetting of the film was observed, which was attributed to the surface having poor interactions with both blocks. For the underlayer with 65\% PS, there are height variations of \(\sim\)4 nm across the field of view. Finally, for the 62\% underlayer, a number of raised features were observed with a height of half of a long period of the polymer, which were characteristics of one block preferentially interacting with the substrate in a film that had a thickness that was incommensurate with the long period of the block copolymer.64

Qualitative analysis of these images suggested that the 65\% PS may be a neutral surface for the PS-b-PMMA (38k-b-37k) with 20\% emim \(\text{NTf}_2\).

To investigate the morphology of the thin film further, the PS-b-PMMA (38k-b-37k) with 20\% emim \(\text{NTf}_2\) on the 65\% PS underlayer was analyzed using GISAXS. In a similar fashion to SAXS, the GISAXS profiles provide information on the morphology present by interpretation of the relative spacings of the diffraction peaks. The primary experimental differences are that the samples are thin films and the beam is directed onto the sample at a grazing angle of incidence. This sample geometry means that characteristic scattering profiles for lamellae are observed only when they are oriented perpendicular to the substrate.28 Figure 6(a) shows a 2-D GISAXS scattering profile, where second- and third-order Bragg peaks are evident at integer multiples of \(q^*\). These peaks are more evident in the sector average shown in Fig. 6(b). This result confirms that the lamellae are oriented perpendicular to the substrate and that the 65\% PS underlayer can act as a neutral layer for blends of 20 volume \% of emim \(\text{NTf}_2\) with PS-b-PMMA.

3.2.2 Tuning lamellae spacing in a thin film

Having identified a neutral surface for one of the blends of emim \(\text{NTf}_2\) with PS-b-PMMA, further experiments were conducted to demonstrate the tunability of the pitch and morphology in the thin film. Figure 7(a) shows high-resolution SEM images of PS-b-PMMA (38k-b-37k) with 0\% (left) and 25\% (right) emim \(\text{NTf}_2\). In both cases, a fingerprint pattern could be observed that was characteristic of lamellae oriented perpendicular to the substrate. The darker contrast corresponds to the PMMA domains and the lighter contrast corresponds to PS domains. It could also be seen that the samples with 0\% emim \(\text{NTf}_2\) had a number of cylinder-like defects, but these are not evident in the sample formulated with 25\% emim \(\text{NTf}_2\). This indicates that defectivity may be lower for IL-containing systems, which may be due to the higher mobility of PMMA chains. However, more systematic analysis is required to support this hypothesis. The insets of the SEM images show fast Fourier transforms (FFTs) that were calculated from the SEM images, which allowed the long period to be estimated. The sample with 0\% emim \(\text{NTf}_2\) had a peak corresponding to a long period of 39 nm, while sample formulated with 25\% IL had a peak corresponding to 45 nm, confirming that the pitch of the lamellae could be tuned by introducing emim \(\text{NTf}_2\) into the PS-b-PMMA formulation. However, the increase observed was significantly less than for the bulk films (Fig. 2), i.e., a 6-nm change in the long period corresponds to a bulk sample with approximately 5.5\% emim \(\text{NTf}_2\). In addition, it would be expected that for a blend with 25\% emim \(\text{NTf}_2\), the morphology should transition

![Fig. 5 AFM height images (20 \(\times\) 20 \(\mu\text{m}\) field of view) of PS-b-PMMA (38k-b-37k) doped with 20\% emim \(\text{NTf}_2\) on three different underlayers, (a) 69\% PS, (b) 65\% PS, and (c) 62\% PS. Film thickness was \(\sim\)1.5 times the long period, i.e., \(\sim\)60 nm.](image-url)
to a cylindrical/hexagonal morphology. One possible explanation for this difference is that the IL is partitioning into the underlayer, which is a statistical copolymer of styrene and methyl methacrylate. Partitioning of IL into the underlayer may also explain why the same underlayer acts as a neutral layer for formulations with 0% and 25% emim NTf₂. This is because emim NTf₂ that partitions into the underlayer would be expected to influence the interfacial interactions that occur with the blend of block copolymer and IL. Nonetheless, we have demonstrated that it is possible to tune lamellar domain size in thin films by blending emim NTf₂ with PS-b-PMMA.

Fig. 6  (a) 2-D GISAXS scattering profile for a thin film of PS-b-PMMA (38k-b-37k) doped with 20% emim NTf₂ on an underlayer containing 65% PS. (b) Sector averaged 1-D GISAXS profile. Both exhibit the characteristic Bragg peaks for lamellae oriented perpendicular to the substrate.

Fig. 7  High-resolution SEM of (a) thin films of neat PS-b-PMMA (38k-b-37k) [left] and of PS-b-PMMA (38k-b-37k) doped with 25% emim NTf₂ [right], (b) thin films of neat PS-b-PMMA (96k-b-36k) [left] and of PS-b-PMMA (96k-b-36k) doped with 25% emim NTf₂. For all SEM images, the darker contrast corresponds to the PMMA domains and the light contrast to PS domains. All samples used an underlayer that had a 65% PS content. The thickness of the BCP films were 60 ± 4 nm. The scale bars in the SEM images are 100 nm. The insets to the SEMs is the FFT calculated from the SEM images.
3.2.3 Tuning morphology in a thin film

Finally, we sought to determine if the thin film morphology of PS-b-PMMA could be transformed by addition of emim \text{NTf}_2. Figure 7(b) shows the high-resolution SEMs of PS-b-PMMA (96k-b-36k) thin films with 0% and 25%. The darker contrast corresponds to PS domains and the lighter contrast corresponds to PS domains. In the absence of emim \text{NTf}_2, a cylindrical/hexagonal morphology was observed, while the formulation with 25% emim \text{NTf}_2 had transitioned to a lamellar morphology. The PS-b-PMMA (96k-b-36k) also exhibits some variation in contrast to the PMMA domains. This can be attributed to the formation of a wetting layer of PS at the air interface for some of the PMMA lamellae. The morphologies are not identical to those observed in the bulk for the same concentrations of emim \text{NTf}_2, which may again be due to some partitioning of the emim \text{NTf}_2 into the underlayer, or could also be a result of a perturbation of the phase diagram due to the increasing significance of the polymer–air and polymer–substrate interfaces in the thin films compared to the bulk. Nonetheless, we have demonstrated that it is possible to transition the thin film morphology of a block copolymer from hexagonal to lamellar by blending with emim \text{NTf}_2.

The initial work on thin films has focused on PS-b-PMMA with domain sizes as small as 39 nm. To be useful for future DSA applications this will also need to be demonstrated for BCPs with smaller domain sizes. The anticipated challenges in achieving this are likely to lie in minimizing the partitioning of the IL into the underlayer, because use of BCPs with smaller domain sizes will also necessitate thinner film thicknesses. One way to achieve this may be to use polymer brushes to generate the neutral underlayer.

4 Conclusions

This study has investigated the changes that occur to the bulk and thin film morphology of PS-b-PMMA when it is blended with varying amounts of an IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (emim \text{NTf}_2). It was found that small amounts of emim \text{NTf}_2 could increase the effective \( \chi \) parameter and could induce order for low-molecular-weight systems, which when neat have \( \chi_N \) values <10.5 (i.e., are disordered). In addition, it was demonstrated that in the bulk it was possible to tune the long period (pitch) of lamellae, or transitions from one morphology to another, simply by adding different amounts of emim \text{NTf}_2. In terms of thin films formulated with 0% to 25% emim \text{NTf}_2, it was demonstrated that lamella oriented perpendicular to the substrate could be obtained using the same underlayer, i.e., a neutral underlayer optimized for PS-b-PMMA with no added emim \text{NTf}_2. Finally, it was demonstrated that tuning of the long period and transitioning of morphologies could also be achieved in thin films. The favorable physical properties of ILs, which include negligible vapor pressure and excellent thermal stability, mean that they can be formulated with BCPs in solution, spin coated, and undergo high-temperature annealing steps. This can all be achieved without conducting additional processing steps and does not require additional infrastructure in the fab, which makes the approach outlined in this study amenable to integration into current preproduction processing steps that have been developed by industry.


Thomas Bennett completed a BSc(Hons) in chemistry at the University of Queensland, Australia, in 2011. He is currently undertaking a PhD on block copolymer ionic liquids for advanced functional material applications, with Associate Professor Idriss Blakely at the Australian Institute for Bioengineering and Nanotechnology. His research interests include polymer and ionic liquid synthesis, block copolymer thin films, and the characterization of these materials via small-angle x-ray scattering, atomic force microscopy, and scanning electron microscopy.

Kevin Pei completed the first year of a bachelor of chemical engineering degree at the University of Queensland in 2013. He carried out a vacation project at the Australian Institute for Bioengineering and Nanotechnology with Prof. Blakely. He is currently continuing his undergraduate studies.

Han-Hao Cheng received his PhD degree from the Department of Electrical and Electronic Engineering, University of Canterbury, New Zealand, in 2009. He was a postdoctoral fellow at Australian Institute for Bioengineering and Nanotechnology (AIBN), the University of Queensland, St. Lucia, Australia, for developing directed-self-assembly-based lithography applications for extreme ultraviolet lithography in collaboration with Intel Corporation between 2009 to 2012. He is now a senior professional officer at the Australian National Fabrication Facility, Queensland node.

Kevin Jack received his PhD from the University of Queensland, Australia in 1996. He undertook postdoctoral positions at Queen's University, Canada and Bristol University, UK, and was a research scientist at the Bristol Colloid Centre until 2004. He is currently a senior research fellow in the Centre for Microscopy and Microanalysis, the University of Queensland. His research interests are in structure-property relations in materials and their advanced characterization by x-ray, neutron, and NMR methods.

Idriss Blakely is an associate professor and an Australian Research Council Future Fellow at the University of Queensland, Australia. There he leads research programs that develop functional polymers and nanomaterials for applications that include lithography, biosensors and biomedical imaging agents. Prior to this, he was a research scientist at Polymerat, an Australian biotechnology start-up company (2000 to 2003). In 2001, he was awarded a PhD in Polymer Science from the Queensland University of Technology.