

Supporting Information:

Solvent Processing and Ionic Liquid Enabled Long-Range Vertical Ordering in Block Copolymer Films with Enhanced Film Stability

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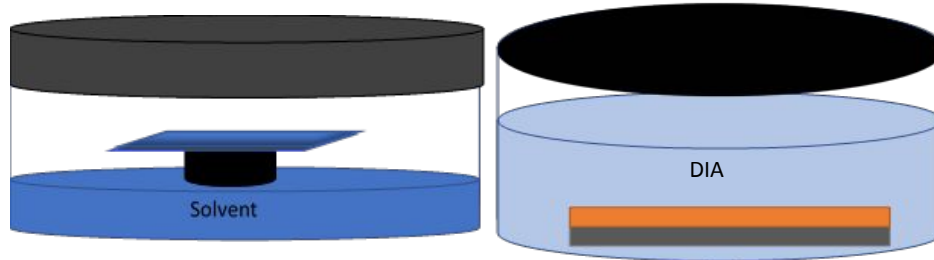


Figure S- 1: Schematic representation of the SVA and DIA setup. The typical DIA or SVA solvent can include non-solvent such as heptane, a good solvent such as toluene, and a ‘selective’ good solvent such as acetone. The choice of the solvent is made to optimize the driving force for ordering (χ), the orientation of the BCP morphology with respect to the substrate, the grain size of the ordered BCP domains obtained after the ordering process has commenced, minimization of local defects in the BCP ordered morphology, enhancing the rate of BCP ordering and the stability of the BCP film against dewetting.

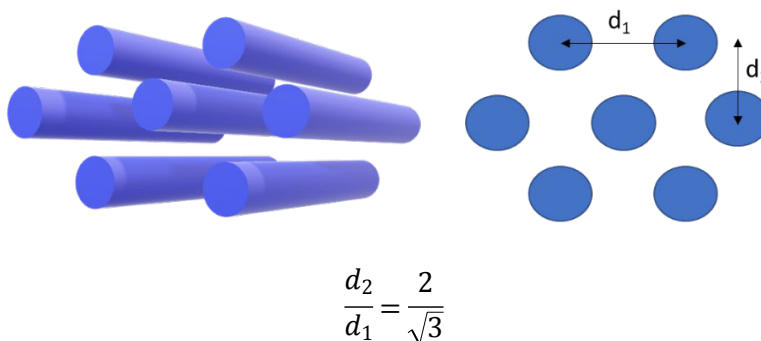


Figure S- 2: Arrangement of 3D cylindrical structure with in-plane dimension d_1 and planar dimension d_2 .

The experimental setup for the SVA and the DIA is seen in fig. S-1. In DIA, the use of a non-solvent, such as heptane, is essential to prevent dissolution. Other solvents used for both DIA and SVA include good solvents such as toluene and selective solvents such as acetone. The acetone is PMMA selective and helps attain parallel lamellae or cylindrical BCP mesophases when the thin films are cast on the silicon surface. Fig. S-2 shows the schematic 3D arrangement of the cylindrical morphology structure. The presence of the $\sqrt{3}$ peak in GISAXS is due to the difference in the in-plane domain length d_1 and d_2 because of the periodic hexagonal structure.

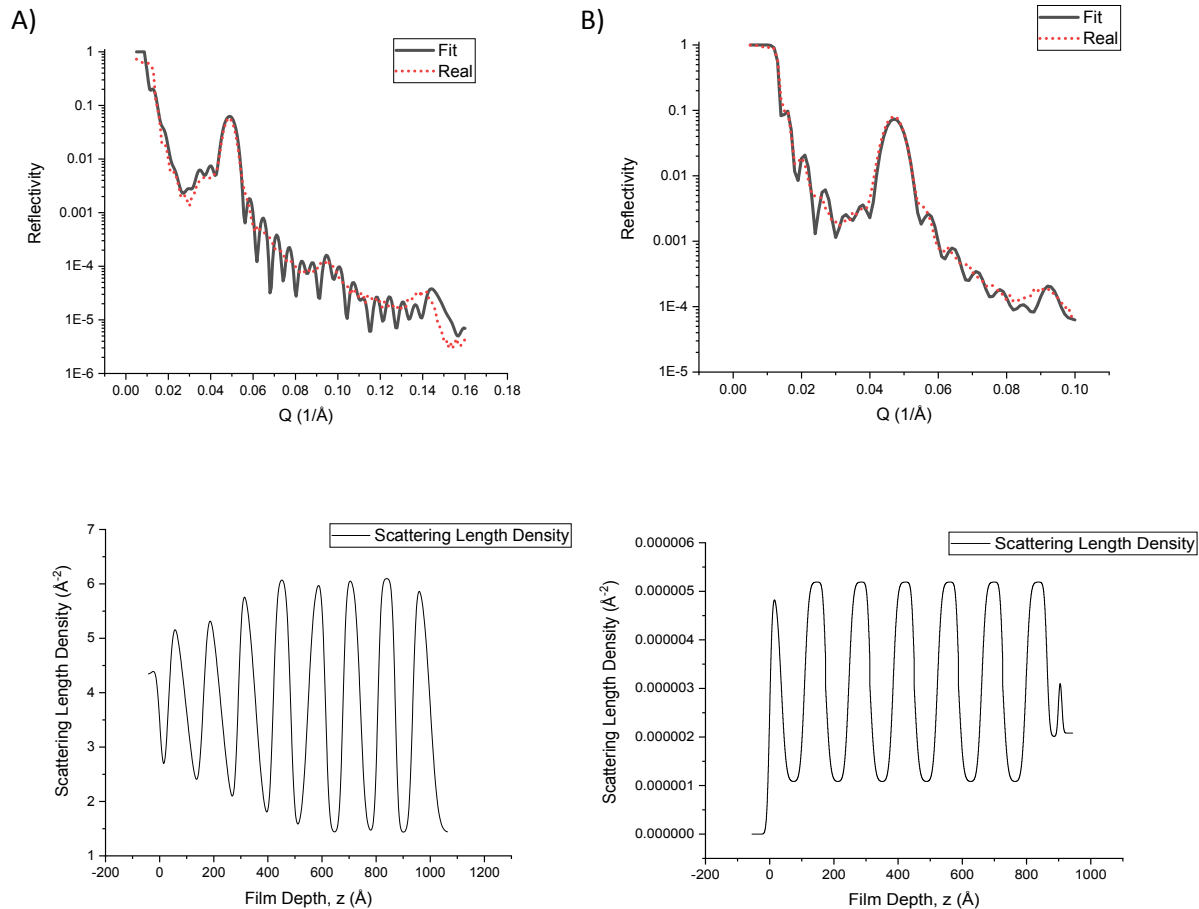
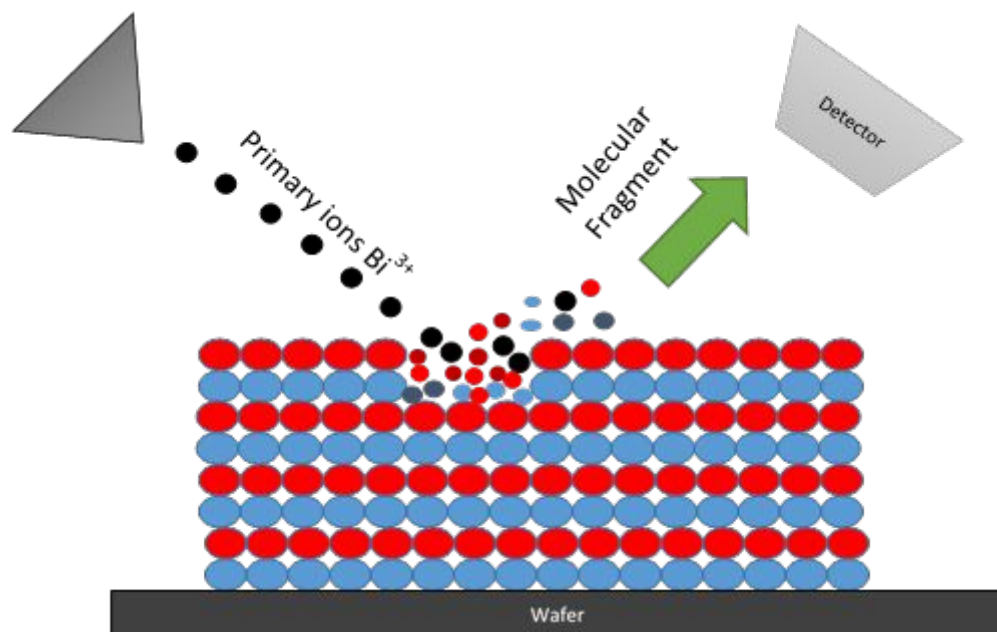


Figure S- 3: NR profile of a dPS-PMMA 19.5k-18.1 k BCP film annealed in a selective DIA solvent mixture for 1 h with A) No IL B) 5% IL. The lamellar profile of IL-containing film is more oriented with less composition fluctuations compared to no IL-containing film.

Fig. S3 shows the neutron reflectivity (NR) profile of the dPS-PMMA 19.5k-18.1k film annealed with DIA in heptane, toluene, and acetone solvent mixture in a volume ratio of 75 : 25: 5. The selective solvent helps the polymer attain a parallel lamella ordering. It was shown by Longanacker et al.¹ that selective DIA ordering can reduce the domain width by about 50% and the interfacial width by up to 27 %. Our finding suggests that ordering orientation and structure improves further if IL is used as an additive in this DIA mixture (figure S-3B). It is emphasized that the selected IL here EMIM TFSI is also soluble in acetone. However, even after DIA, IL still remains in the

polymer after DIA and as such the IL and DIA mixture has a much greater influence in orientation control and tuning the Flory-Huggins interaction parameter, χ , than annealing the film with DIA alone. It's also manifested from the fact that the DIA without IL (fig. S-3A) saw a domain length reduction from 27.6 nm to 14.2 nm and an interfacial width reduction from 53.6 Å to 44 Å, compared to thermal annealing. In contrast, DIA with IL saw a domain length reduction to 13.8 nm and interfacial width reduction to 40 Å (fig. S-3B). Therefore, DIA with IL achieved a domain length reduction of 50% and interfacial width reduction of 34.4 %, higher than annealing the films in DIA alone without any IL. This clearly suggests that DIA with an IL induces a higher thermodynamic and kinetic driving force to attain equilibrium orientation, resulting in a relatively low defect density film, with larger BCP 'grains' of common BCP ordered phase orientation.

A)



B)

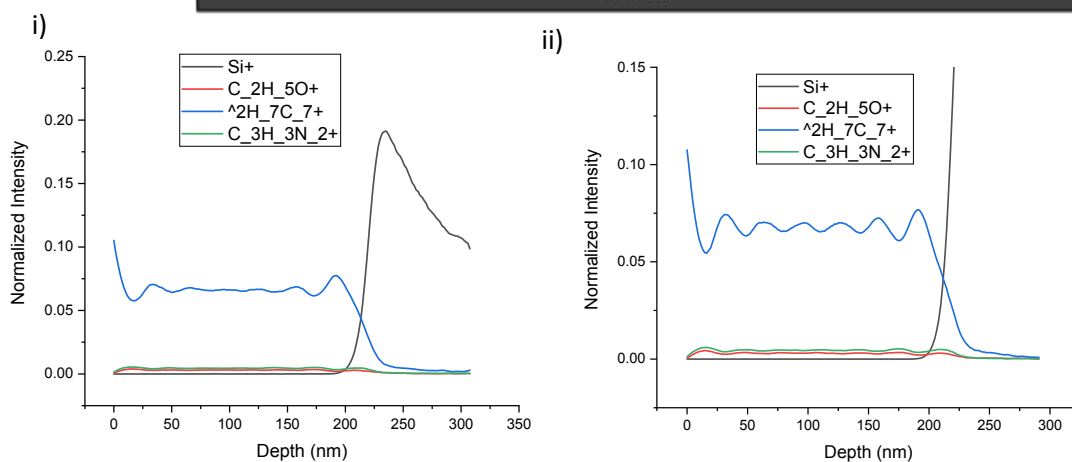


Figure S- 4: A) Schematic of time of flight- secondary ion mass spectroscopy (ToF-SIMS) procedure. B) ToF-SIMS profile of a dPS-PMMA 47.5 k-51 k BCP film of (200 to 220) nm annealed in selective DIA mixture for 3 h with i) No IL ii) 5% IL. The profile became more sinusoidal with the IL solvent.

Fig. S-4 A shows the schematic of the ToF-SIMS methodology used to etch a thin layer and study the chemical composition of the films. Fig. S-4 B shows the positive ToF-SIMS profile of the dPS-PMMA 47.5k-51k BCP films of about 200 nm thickness. It can be seen without IL, fig. S-4 B i), the ordering propagation through the films is much weaker relative to the film containing 5 % IL

(fig. S-4 B ii). The orientation has improved with long-range sinusoidal order propagation as seen here in this high Mw lamellar system of about 100k that is very tough to order using thermal annealing. Similar results are also seen in fig. S-5, where PS-PMMA films of much higher M_w of 65k-62.5k (127.5k), are almost impossible to order in the thickness of 300-400 nm using thermal annealing, show superior order propagation using DIA. Moreover, DIA with IL shows even better sinusoidal profile development suggesting a higher degree of long-range order with lower defect density when annealed for 4 to 10 hours.

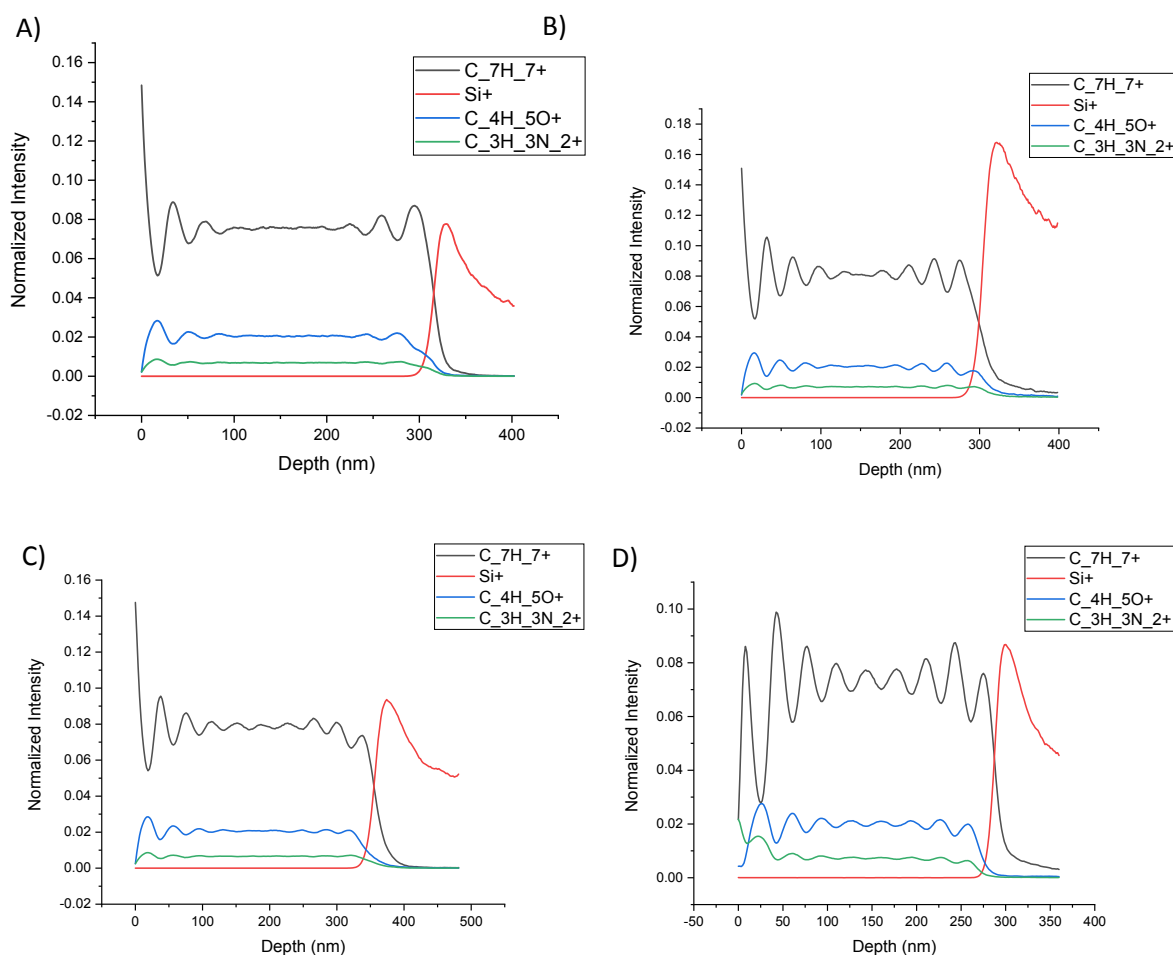


Figure S- 5: The ToF-SIMS depth analysis of PS-b-PMMA 65k-62.5k BCP films processed with a heptane, acetone toluene mixture in 75:25:5 volumetric ratio annealed for 4 h. A) No IL) B) with 5 % IL in films, and 10 h C) No IL D) with 5 % IL in the films.

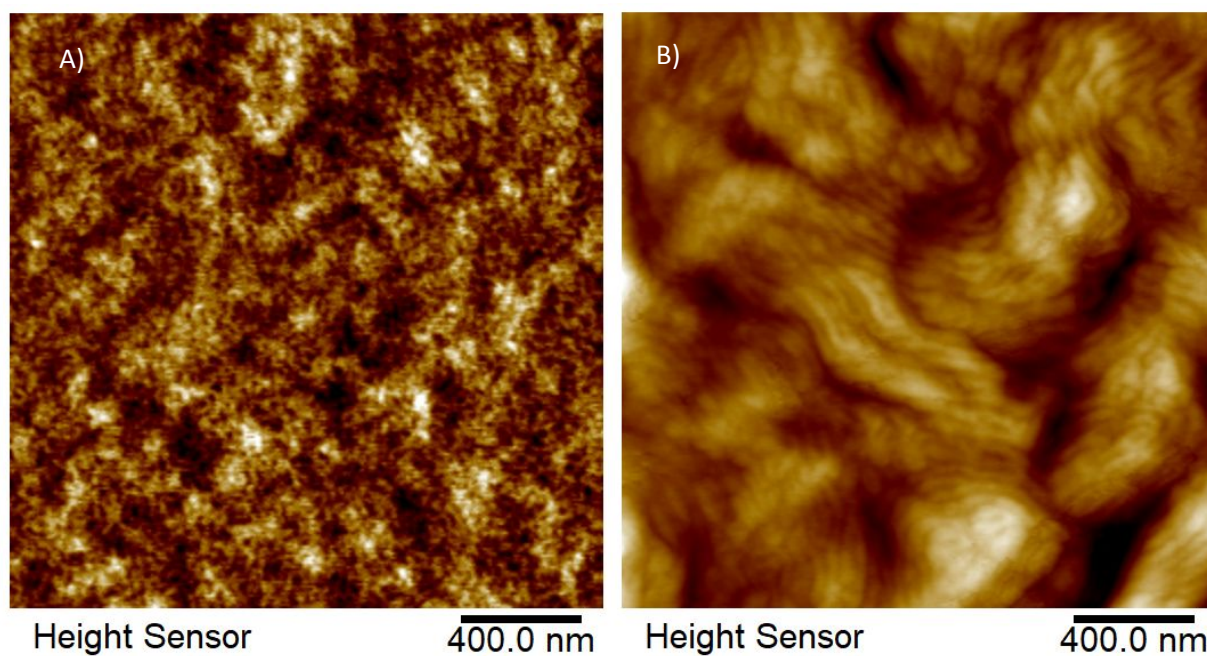


Figure S- 6: The UV etching AFM height profile of PS-b-PMMA 33k-33k BCP films processed with heptane, toluene mixture in 3:1 volumetric ratio, annealed for 30 mins for (60 to 70) nm thick films after etching removal at a depth (35 to 40) nm using a 193 nm UV lamp for 12 mins with A) No IL B) 10 % IL

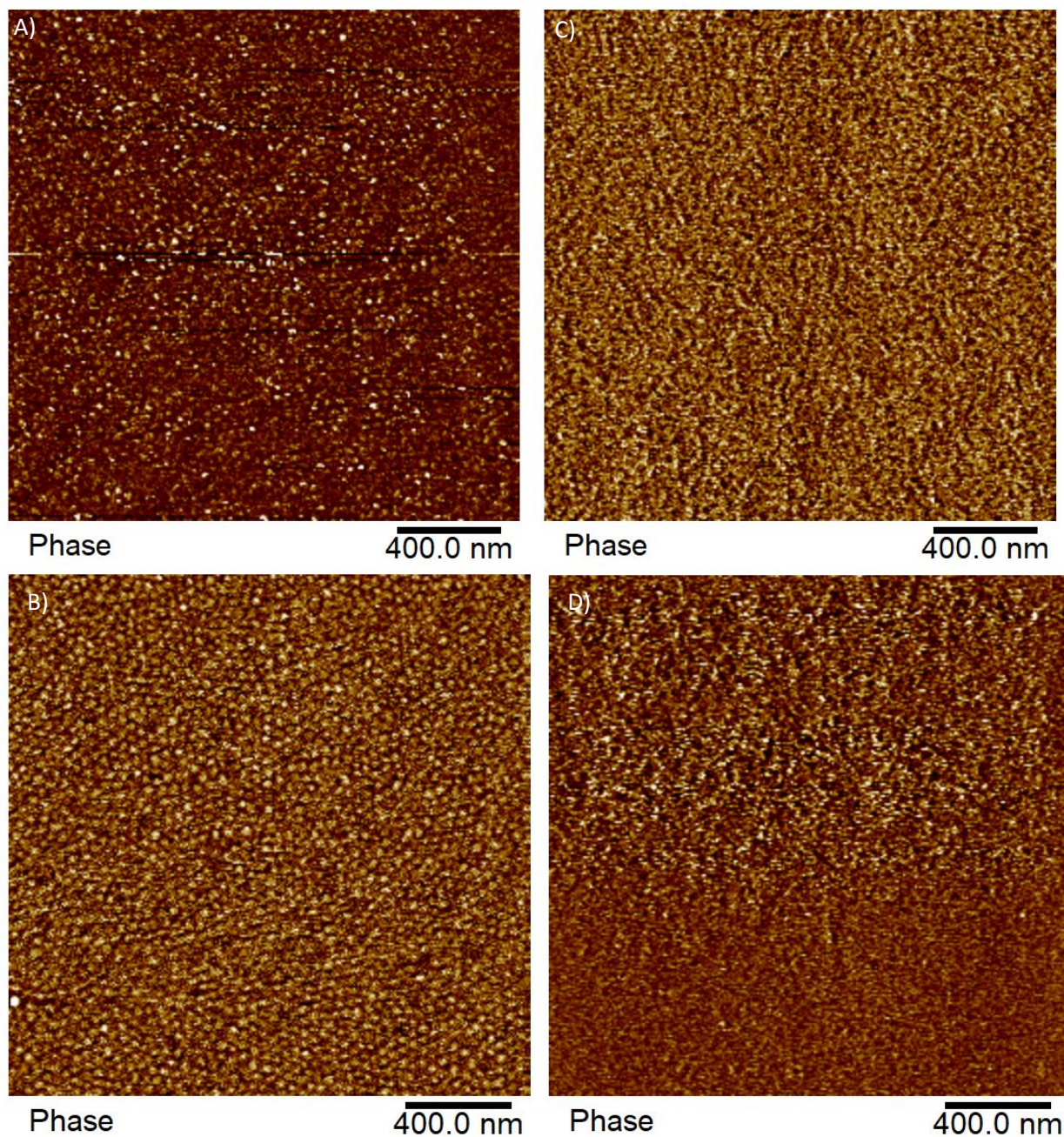


Figure S- 7: The AFM images of the PS-b-PMMA 55k-22k of BCP films exhibit cylindrical morphology. The film was thermally annealed at 170 °C for 24 h with an initial film thickness of 70-80 nm thickness with A) No IL B) With 10% IL. The films were then etched in UVO for 15 mins to remove about (40 to 45) nm of the polymer for C) No IL and D) 10% IL containing films.

Fig. S-6: shows the AFM height profile of the UV ablated films for the thickness of 60-70 nm after etching for 12 min to remove about (35 to 40) nm of the film after DIA in a neutral solvent with no IL and with 10 % IL. It can be seen from S-6A with no IL that there is no bulk perpendicular order visible, but with IL, long-range perpendicular order is still visible, confirming the propagation of vertical order in IL-containing films. Fig. S-7 shows the AFM phase image of the PS-PMMA cylindrical 55k-22k morphology annealed for 170°C for 24 h. Since the PS block is far above the entanglement molecular weight, such BCPs are not easy to order using thermal annealing. Although IL shows slightly better ordering at the surface than no IL-containing films, such ordering is present only for a few tenths of nanometer on the surface. It was confirmed using UV ablation of the films to remove (25 to 60) % of the films. It can be seen in fig. S-6 that there is almost no bulk ordering present with or without IL. However, when annealed using DIA, these films display complete ordering as revealed by GISAXS, ToF-SIMS experiments, and UV ablation in Fig. S-6.

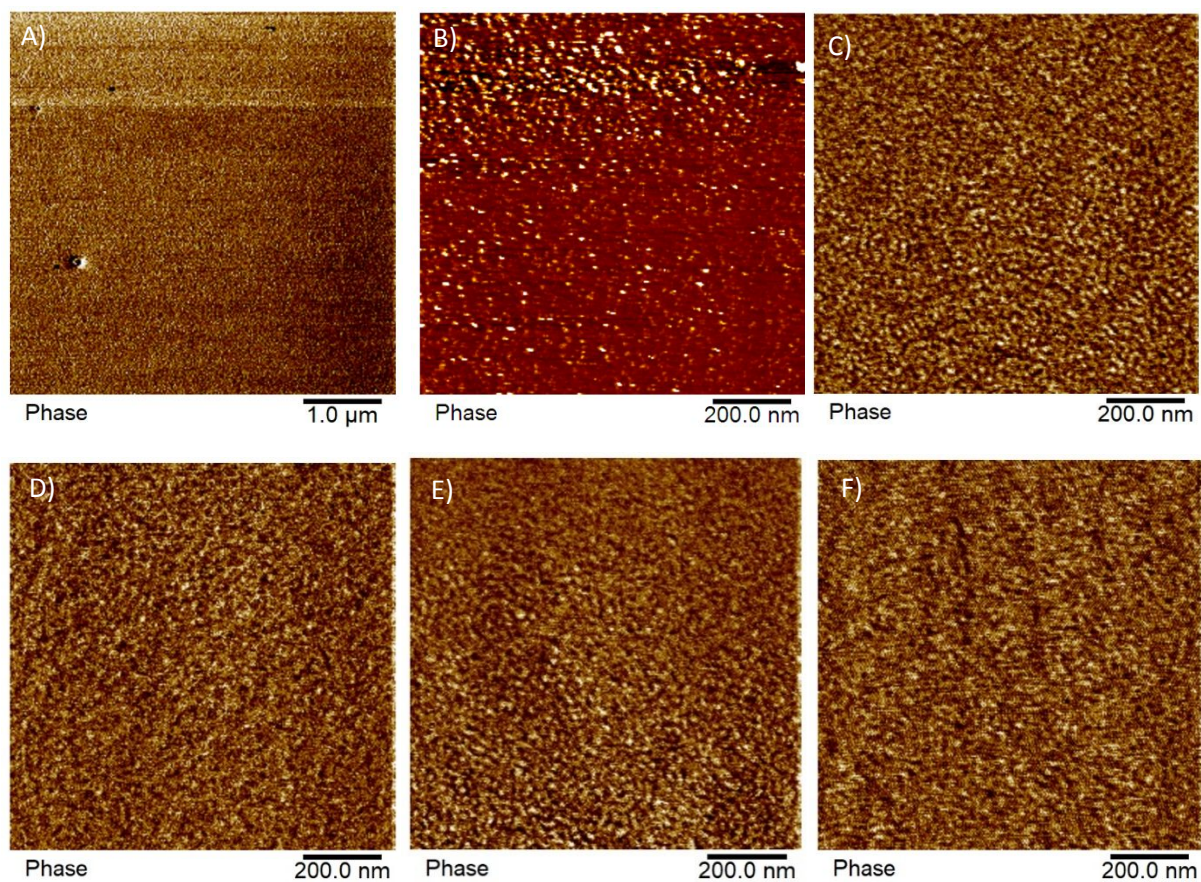


Figure S- 8: The AFM images of the PS-PMMA 10k-10k BCP film exhibiting a lamellar morphology. The film thickness is about (30 to 40) nm, and the film was cast on a silicon surface (A-C) and on neutral surface (D-F) with A, D) No IL B, E) With 5 % IL C, F) With 10 % IL.

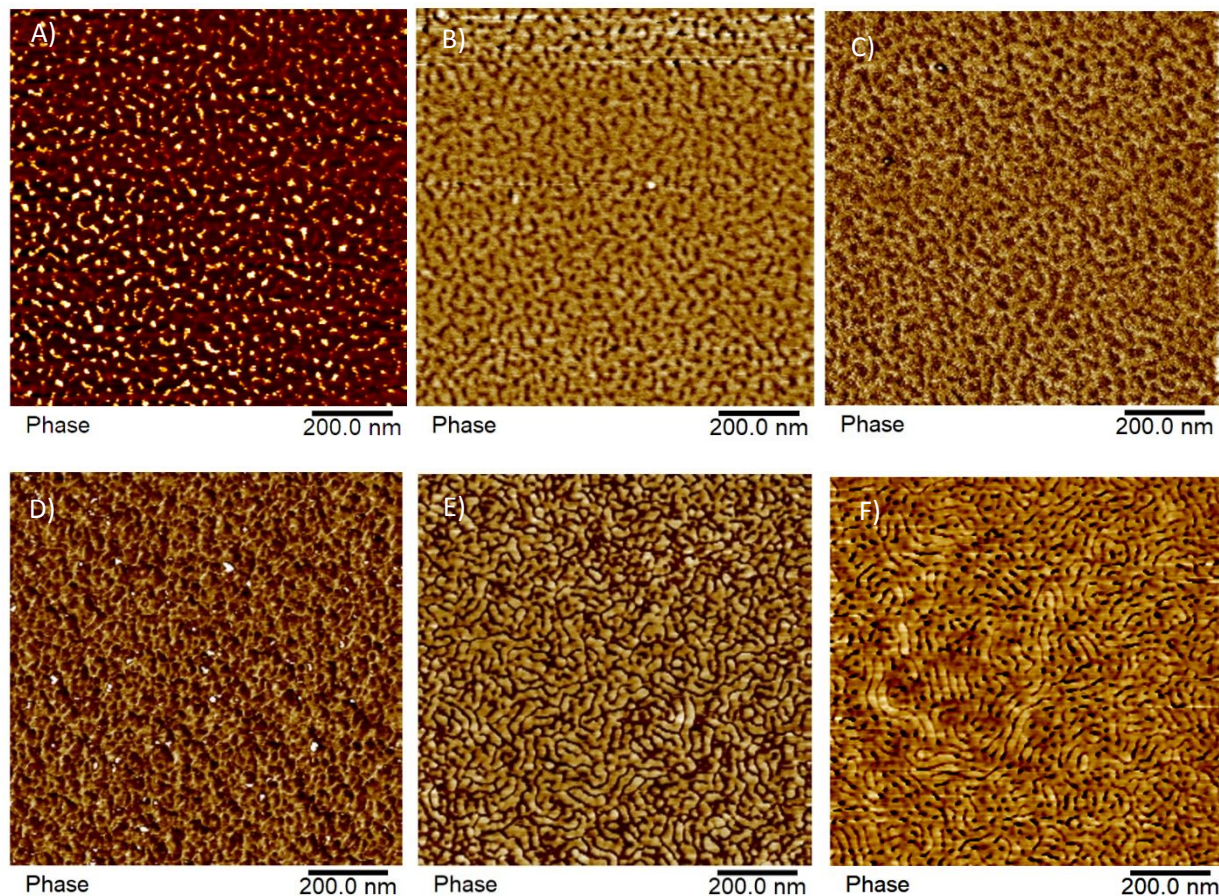


Figure S- 9: The AFM images of the PS-b-PMMA 10k-10k of lamellar morphology of about (30 to 40) nm thickness after DIA for 30 mins in toluene and heptane mixtures in a ratio of 1 to 3 volume ratio , on silicon surface (A-C) and on neutral surface (D-F) with A, D) No IL B, E) With 5 % IL C, F) With 10% IL

Fig. S-8 shows the as-cast films of PS-PMMA 10k-10k, lamellar system as-cast using flow coating of thickness between (30 to 40) nm or (1 to 3) L_o on a silicon substrate and neutral substrate with 0, 5, and 10% IL by mass. It's seen that some level of vertical lamellae develops in films containing IL, although not very long-range (see fig. S-8 C and F). After performing DIA for 30 mins in the toluene and heptane 1 to 3 mixture, as seen in Figure S-9, vertical lamellae are visible in IL-containing films. Very short-range vertical structure exists in films containing no IL, but the range improves a lot as IL is added. It can be seen in fig. S-9 that the best ordering has been achieved using 10% IL-containing films on the neutral substrate after DIA. The average domain size

obtained in this film is about 23 nm with a half domain length of 11.5 nm in the 10 % IL-containing films having a significant degree of swelling.

References

- [1] M. Longanecker, A. Modi, A. Dobrynin, S. Kim, G. Yuan, R. Jones, S. Satija, J. Bang, and A. Karim, “Reduced domain size and interfacial width in fast ordering nanofilled block copolymer films by direct immersion annealing,” *Macromolecules*, vol. 49, no. 22, pp. 8563–8571, 2016.