

Abstract

Block copolymer (BCP) thin films prepared by dip-coating are increasingly investigated, owing to the many promising application areas, the facility, and industrial scalability of this technique. Yet, the effect of different dip-coating parameters on BCP nanostructure formation is still underdeveloped and the results of previous literature are limited to few block copolymers. Here, we study the effect of withdrawal rate and solvent selectivity on the morphology evolution of dip-coated polystyrene-*b*-poly(ethylene oxide) thin films by applying a wide range of dip-coating speeds and altering the volume ratio of the tetrahydrofuran – water solvent system. The dip-coated films were characterized using atomic force microscopy and ellipsometry. The nanodomain morphology, its feature sizes, its spanning, and degree of ordering were investigated with regard to different dip-coating parameters. Notably, we have obtained a hexagonally-packed BCP pattern with long-range order without the need of post-annealing processes. Overall, a solid understanding of the parameters affecting the formed surface patterns and their interplay was attained and explained, extending the knowledge of this field to more materials.

Materials and methods

A 10 mg/ml polymer solution was obtained by dissolving PS-*b*-PEO in solvent of pure THF (V_0) or THF-water mixtures (2% (V_2), 5% (V_5), and 10% (V_{10}) water by volume). The Si substrates were dip-coated from the polymer solution at various dip-coating speeds prior to characterization steps.

Results

Evolution of PS-*b*-PEO thin film morphology

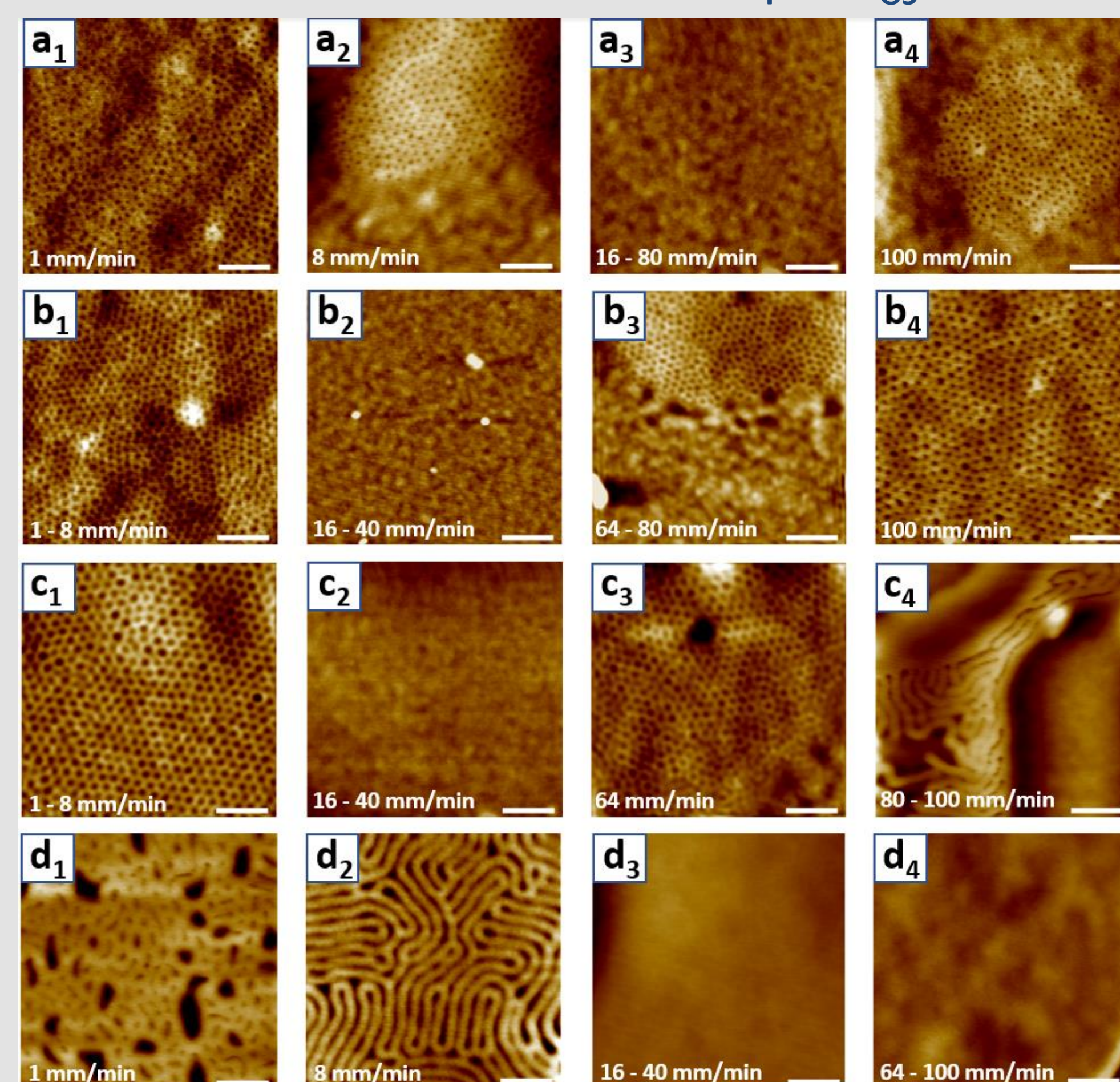


Figure 1. Representative AFM height images of films dip-coated from 10 mg/ml PS-*b*-PEO solutions containing varying contents of water in THF: (a₁ – a₄) V_0 , (b₁ – b₄) V_2 , (c₁ – c₄) V_5 and (d₁ – d₄) V_{10} . The white bar represents a scale of 200 nm.

Table 1. The type and dimensions of the surface patterns observed in the investigated BCP films.

Solvent used	Surface patterns	Nanodomain size (nm)
V_0	Dots	12.4 ± 1.5 (a ₁)
		11.3 ± 0.8 (a ₂)
		11.0 ± 0.8 (a ₄)
V_2	Dots	16.2 ± 1.6 (b ₁)
		16.0 ± 1.1 (b ₃)
		19.4 ± 3.3 (b ₄)
V_5	Dots (1 – 80 mm/min)	27.0 ± 2.1 (c ₁)
		26.1 ± 1.8 (c ₃)
	Stripes (100 mm/min)	32.9 ± 2.6 (c ₄)
V_{10}	Mixtures of dots and stripes (1 mm/min)	37.2 ± 1.6 (d ₂)
	Stripes (8 mm/min)	

Effect of film thickness

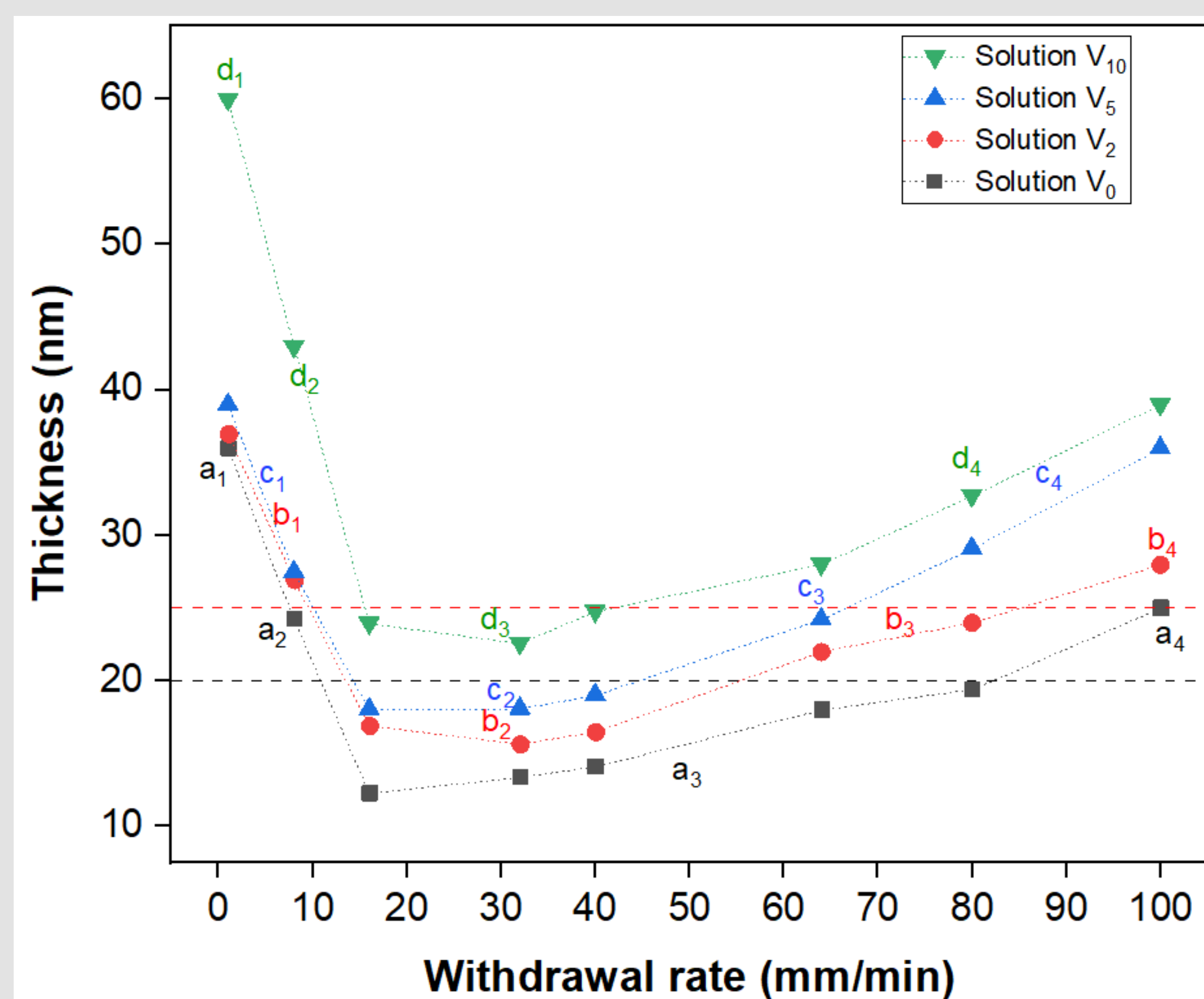


Figure 2. Relationship between film thickness and withdrawal rate for PS-*b*-PEO films dip-coated from solutions of different water contents in THF. In the area between the dashed black line and dashed red line, films with island-like regions containing dot nanodomains were observed.

Table 2. Physical properties of the solvents used and their interaction with PS and PEO blocks.

Solvents	Vapor pressure (mmHg)	Surface tension (dynes/cm)	Viscosity (cP)	Solvent interaction parameter of PS block	Solvent interaction parameter of PEO block
THF	162	26.4	0.53	0.35	0.36
Water	24	72	0.89	4.40	1.26

In the viscous drag regime (>40 mm/min), there is a clear trend of film thickness increasing with greater water content in the solution coated from. In this regime, the thickness of the created films depends on the viscous drag force of the solution.^[3] The intermediate regime (16 – 40 mm/min) showed the same trend of increasing film thickness with increasing water content in the solution.

Effect of solution composition

Table 3. Hydrodynamic radius and the polydispersity index of the PS-*b*-PEO BCP structure in different solvent systems.

Solvent used	V_0	V_2	V_5	V_{10}
Hydrodynamic radius of the BCP, (nm)	8.00	10.77	10.89	16.07
Polydispersity	0.253	0.223	0.213	0.244

The DLS result clearly demonstrates the proportional expansion of PS-*b*-PEO structure with the amount of added water. This further indicates that a solution with greater water content does indeed preferentially interact with the PEO block, leading to preferential swelling during film formation and a greater apparent volume fraction of PEO in the dried film.

Lateral order of the pattern

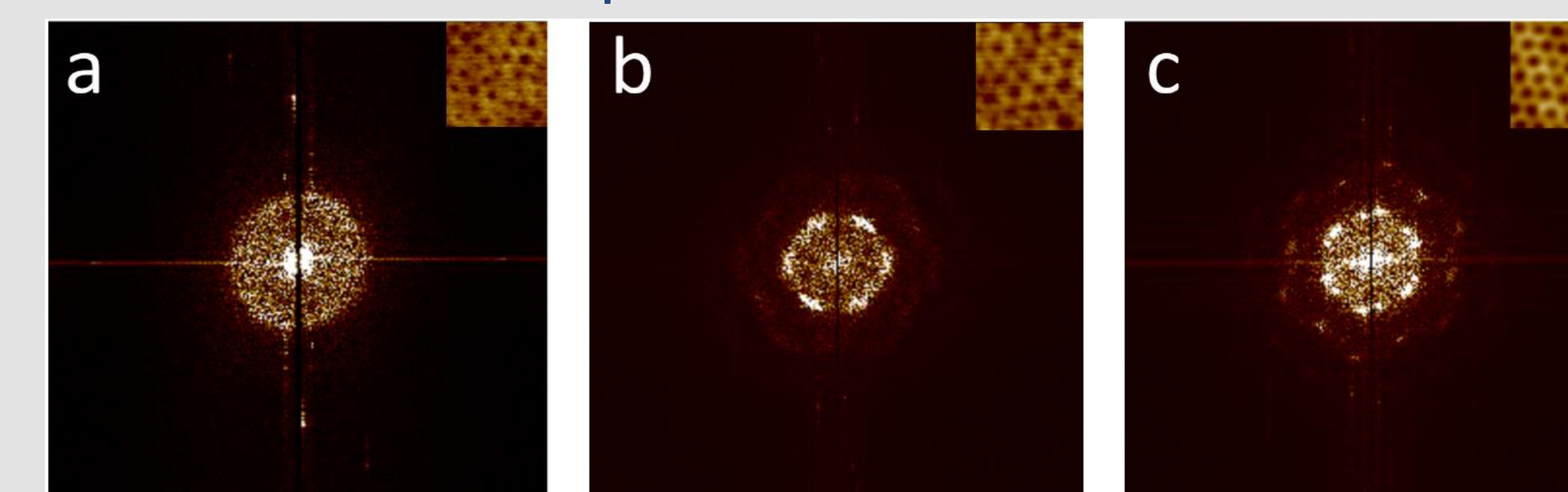
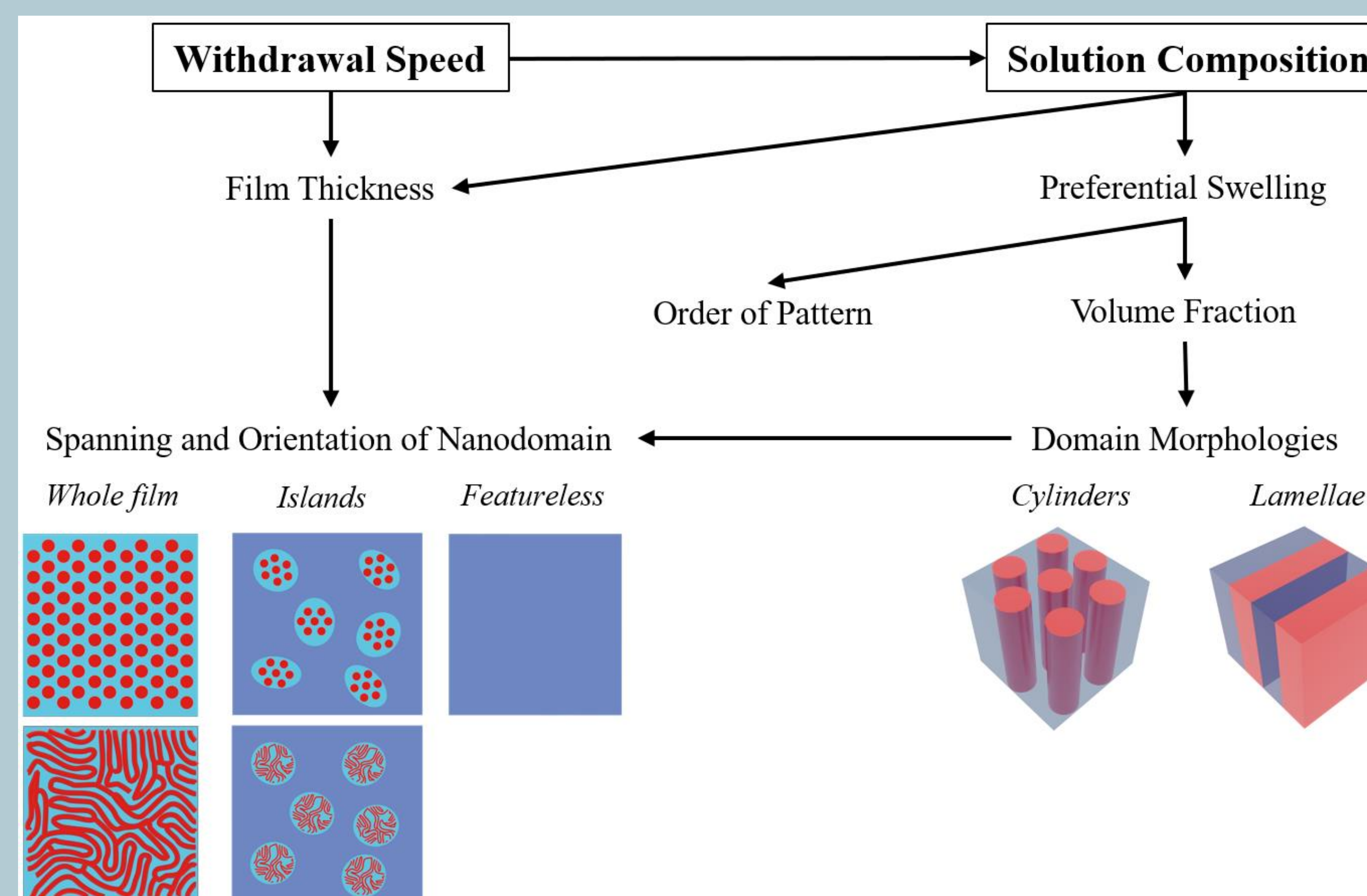


Figure 3. Fast Fourier transform (FFT) of AFM images for the evaluation of the ordering of the cylinders formed from different solutions: (a) V_0 (1, 8 and 100 mm/min), (b) V_2 (1 – 8, 64 – 80 and 100 mm/min) and (c) V_5 (1 – 8 and 64 mm/min).

A greater solvent selectivity, and specifically adding a solvent selective for the minor block, can greatly enhance the ordering of BCP domains during solvent annealing.^[4] An effect similar to solvent annealing was likely observed for our experiments, since the addition of water did not only increase the selectivity of the solvent towards the minor block, but also increased the overall evaporation time.

A general theory to understand the effect of various parameters



❖ The film thickness that is governed by the withdrawal speed and the evaporation rate of the solvent, decides the spanning and orientation of the nanodomain.

❖ The preferential swelling i.e. solvent selectivity, which is determined directly by the solvent composition and indirectly by the evaporation rate that can alter the solvent evolution upon withdrawing, dictates the type of nanostructure.

❖ The selectivity toward the minor block and the increase in overall evaporation time when water is added account for the enhanced ordering of the nanodomain.

References

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