

## Highly ordered honeycomb pattern of surfactant-free bio-compatible film via improved phase separation method

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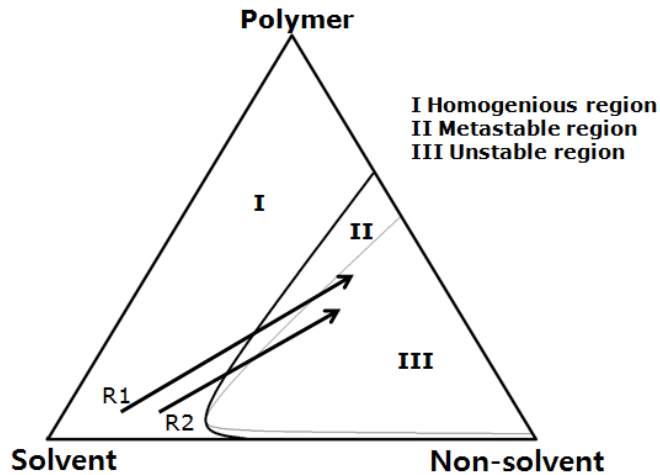
### Experimental Section

The PLA was received from NatureWorks (USA) and dried in a vacuum oven at 40°C before use. Copper foil (99.8% pure; thickness 25 µm) was obtained from Sigma-Aldrich. Copper substrates were washed with dilute acetic acid and distilled water followed by blow-drying in nitrogen gas prior to use. Chloroform (anhydrous, with amylenes as stabilizer, ≥99%), methanol (anhydrous, 99.8%), and anisole (anhydrous, 99.7%) were purchased from Sigma-Aldrich and used as received.

The solution containing 3 w/w% PLA in anisole was prepared and kept stirring for one day to obtain a homogeneous solution. Polymer films were coated onto copper substrates by bar-coating or spin-coating. The thickness of the films were controlled using different bar numbers or changing the rotational speed of spin-coater. The binary mixtures of solvent/non-solvent were prepared by mixing pre-determined volumes of chloroform and methanol, and subsequently stirring for one day before use.

The honeycomb-patterned PLA film was prepared by simply dipping pre-coated PLA on copper substrate into the solvent-mixture of chloroform and methanol; using an E-flex dip-coater (**Supporting Information, Figure S1**). The optimum dipping procedure was: dipping rate of 50 mm/minute, pulling rate of 60 mm/minute and retention time of samples in solvent 5 sec. Subsequently, the samples were left under ambient conditions to completely evaporate all the residual solvents. To provide precisely controlled air-humidity and temperature, we used a Humidity and Temperature chamber (TH-TG-1000, Jeio Tech) (**Supporting Information, Figure S2**).

The morphology of the patterned samples was characterized by field-emission, scanning-electron microscopy (FESEM, JEOL, JSM-7000F, Japan) and atomic force microscope (AFM, Park Science Instruments Autoprobe CP). The elemental analysis was performed by an energy-dispersive X-ray spectrometer.



**Scheme S1.** Schematic representation of a typical polymer–solvent–non-solvent ternary phase diagram.

Arrow R1 represents schematically the concentration path followed by the polymer solutions with low non-solvent content, and R2 with higher non-solvent content. When the two solvents evaporate from the solution surface, the concentration path goes through a metastable region to form nuclei and grow during the non-solvent rich phase (polymer lean phase) subsequent vitrification in the polymer-rich phase stabilizes the forming structures.

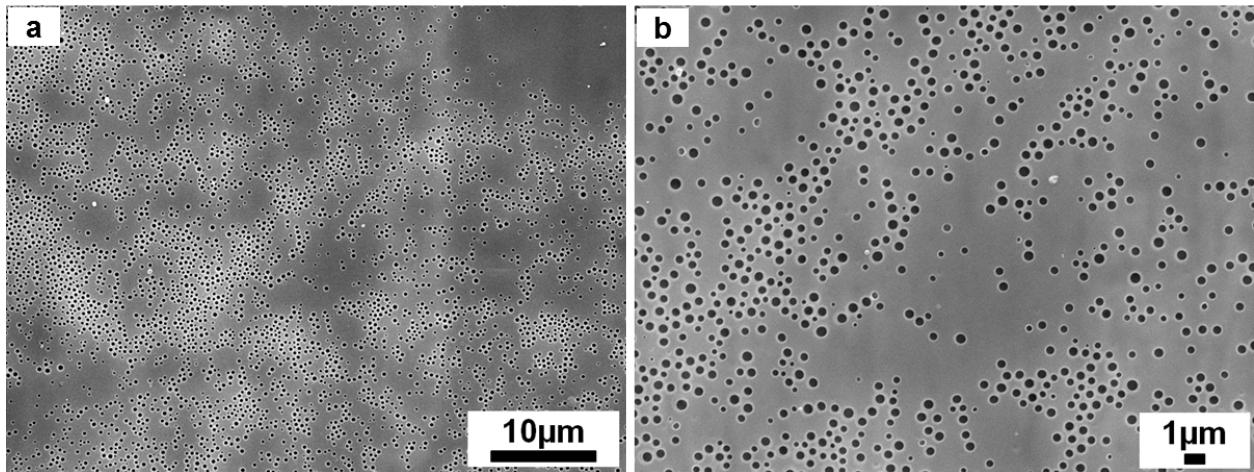
With concentration path R1, the phase separation occurs at lower polymer concentration, and with concentration path R2, this phenomenon occurs at higher polymer concentration. This means that with higher non-solvent content, the phase separation appears at lower viscosity; which is beneficial for growth during the non-solvent rich phase. Thus, the pores become larger.



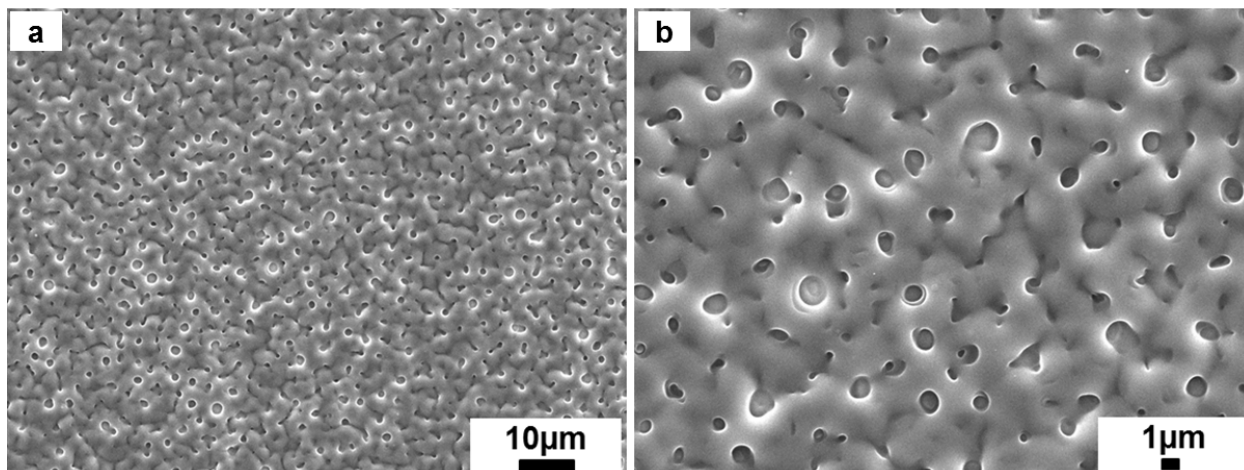
**Fig. S1** E-flex dip-coater.



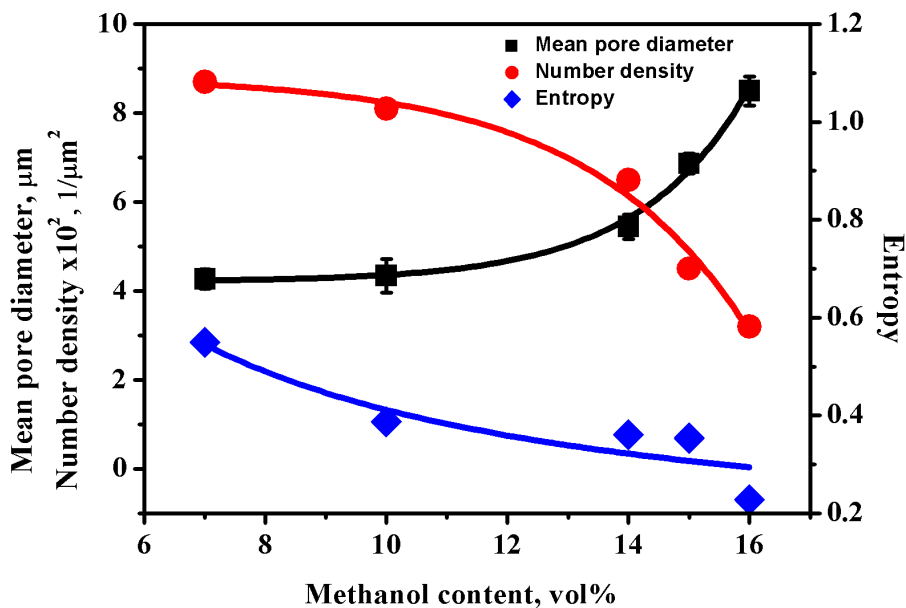
**Fig. S2** Humidity and Temperature chamber.



**Fig. S3:** SEM image of surface of patterned film prepared with pure chloroform, (a) low magnification and (b) high magnification (temperature 20°C and RH 60%).



**Fig. S4** SEM image of surface of patterned film prepared in dry nitrogen gas, (a) low magnification and (b) high magnification (solvent ratio 85-15 and temperature 20°C).



**Fig. S5** Correlation between methanol content and mean pore diameter (black), number density (red) and entropy (blue). The lines are meant as guide to the eye.

The pore-size and the degree of pattern order (conformational entropy,  $S$ ) were quantitatively characterized using ImageJ software. The average pore size ranged from 4  $\mu\text{m}$  up to 8.5  $\mu\text{m}$  in diameter and increased with increasing non-solvent content, resulting in a decrease in the number density of pores. The shape of the micro-pores changes from round to hexagonal. We attribute this phenomenon to the contribution of the non-solvent rich phase, in forming the pores and controlling pore-size. As the methanol content increases, the concentration path would reach binodal curve at lower polymer concentration (Supporting Information, Scheme S1). This means that phase separation would occur at low viscosity of the solution, which benefits the growth of methanol rich droplets, and enables formation of

larger pore sizes. The analysis of Voronoi constructions was performed and the conformational entropy  $S$  was calculated according to the literature [S1]. As shown in Fig. 3, the entropy of patterned films with 7-16% methanol content, showed quite small values (less than 0.5) in comparison with the value (1.71) obtained for the case of a random distribution (a perfectly ordered array has an entropy close to zero). Furthermore, the entropy values of our results are much lower than (0.77 - 0.82) several other recent reports, although they needed to use surfactant for the formation of PLA patterned film.

#### References

[S1] A. Steyer, P. Guenoun, D. Beysens and C. M. Knobler, *Phys. Rev. B*, 1990, **42**, 1086-1089.