Supporting Information

Enhancing the Directed Self-assembly Kinetics of Block Copolymers Using Binary Solvent Mixtures

Woon Ik Park[1†], Young Joong Choi[2†], Je Moon Yun[1], Suck Won Hong[3], Yeon Sik Jung[4], and Kwang Ho Kim[1,2*]

[1]Global Frontier R&D Center for Hybrid Interface Materials (HIM), Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 609-735, Republic of Korea

[2]School of Materials Science and Engineering, Pusan National University (PNU), Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 609-735, Republic of Korea

[3]Department of Cogno-Mechatronics Engineering, Pusan National University (PNU), Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 609-735, Republic of Korea

[4]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST) 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

[†]These authors contributed equally to this work.

[*] Corresponding authors, Email: kwhokim@pusan.ac.kr (K.H.K.), TEL: +82-51-510-3391

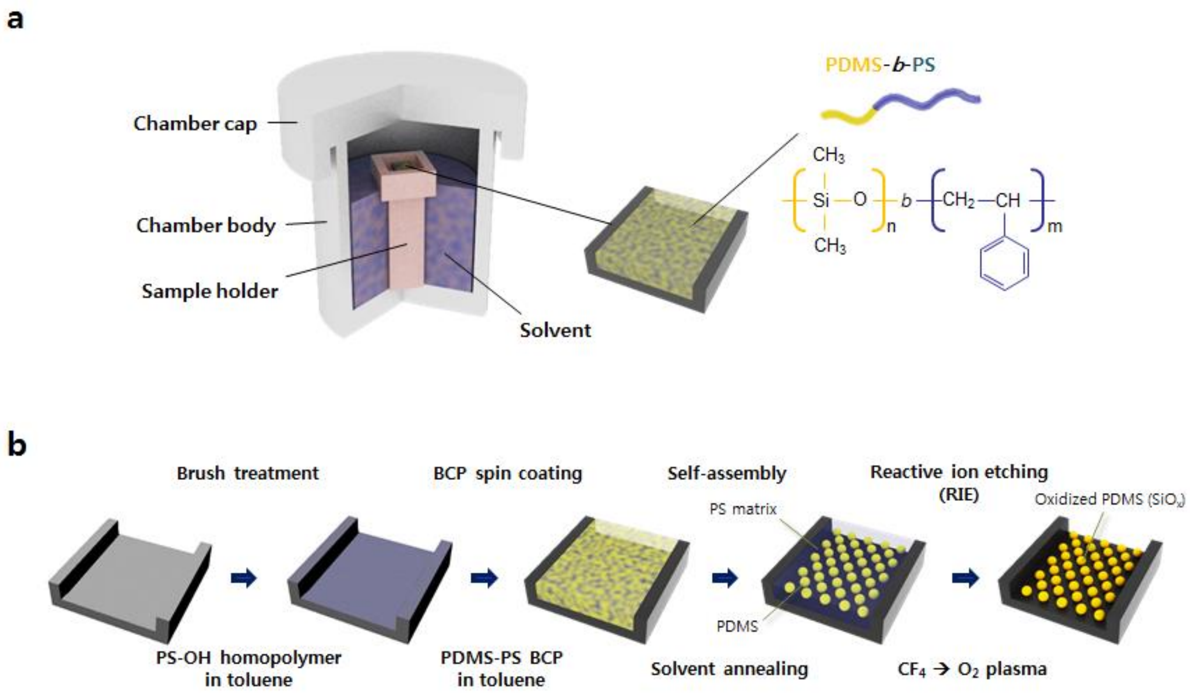

Figure S1. Schematic for an experimental setup of solvent vapor annealing and process sequence for directed self-assembly of BCP via solvent annealing. (a) Experimental setup for solvent vapor annealing of BCP thin film in the chamber filled with solvent. (b) Process sequence for DSA of BCP using solvent annealing.

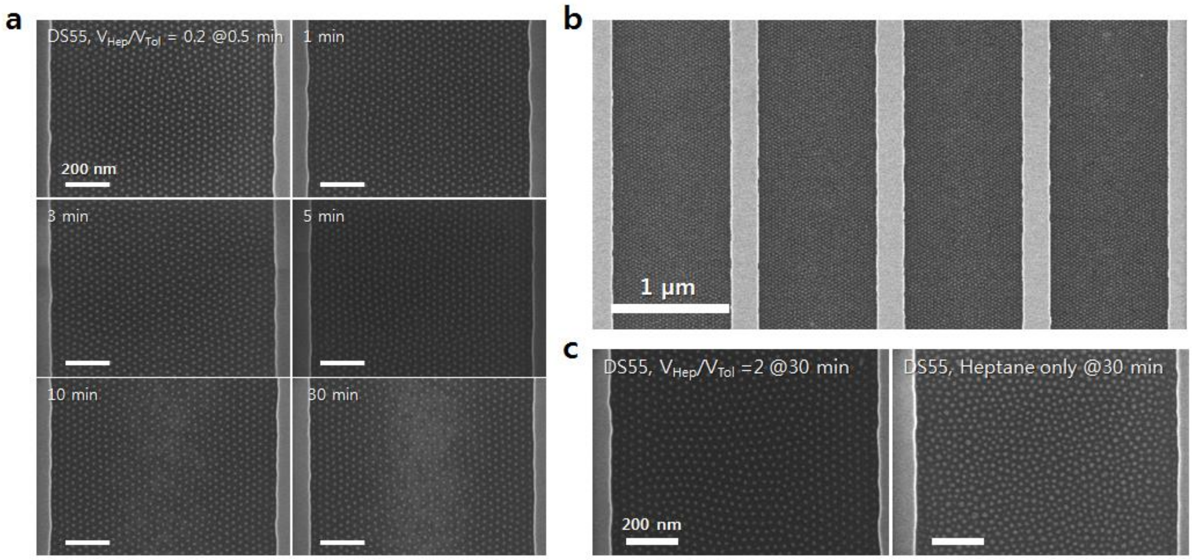

Figure S2. Self-assembled morphologies of DS55 thin film. (a) Time-evolution of DS55 morphologies at V_{Hep}/V_{Tol} = 0.2, showing well-organized dot patterns in 1 minute. (b) SEM image of self-assembled dot pattern formed over the large area. (c) Poorly ordered dot patterns at V_{Hep}/V_{Tol} = 2.0 (left) and pure heptane (right) after long annealing time (30 min). In spite of the long annealing time, excessive addition of heptane to toluene did not produce well-ordered BCP pattern.

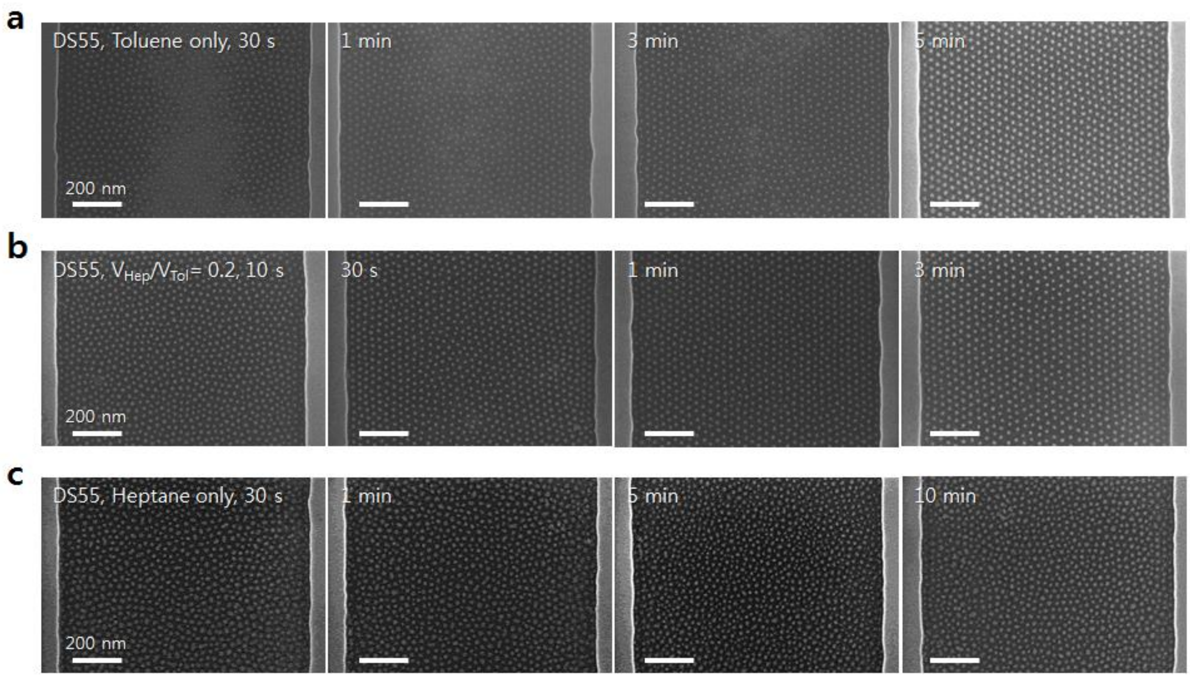

Figure S3. Time-evolution of DS55 BCP morphology. Self-assembled dot pattern annealed at (a) pure toluene for 30 sec, 1min, 3 min, and 5 min, (b) V_{Hep}/V_{Tol} = 0.2 for 10 sec, 30 sec, 1 min, and 3 min, and (c) pure heptane for 30 sec, 1 min, 5 min, and 10 min. A binary solvent of heptane and toluene enables more rapid microphase separation of BCP compared to pure toluene and pure heptane.

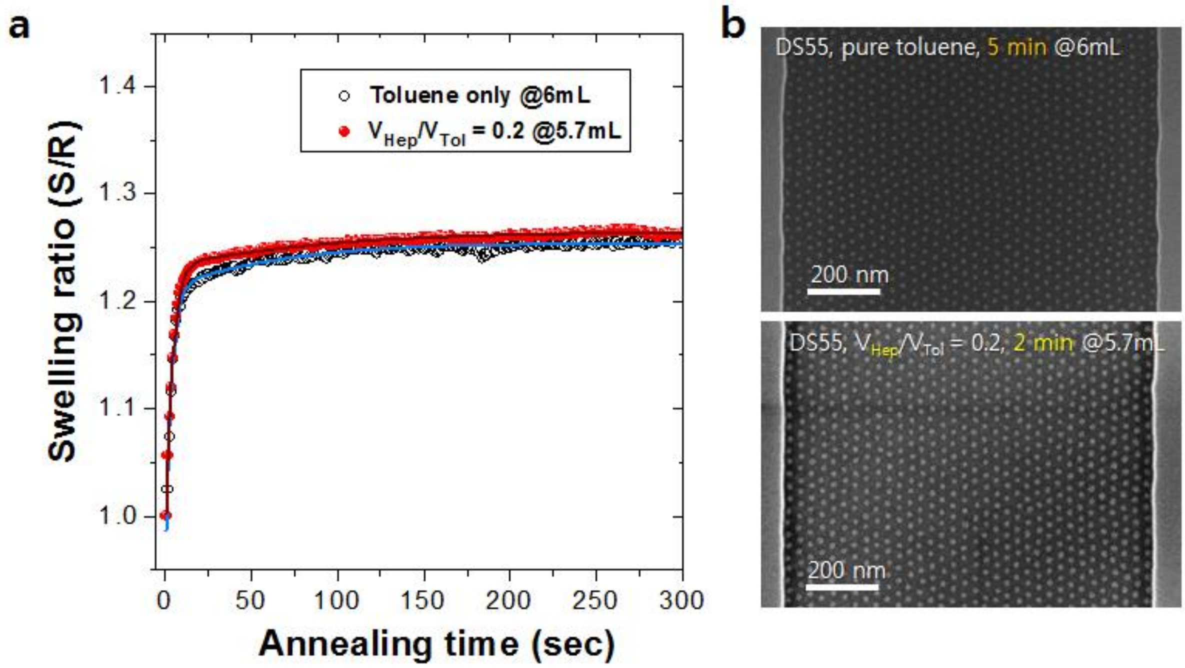

Figure S4. Comparison of SRs for a DS55 BCP thin film annealed at pure toluene and binary solvent. (a) SR curves of DS55 annealed at pure toluene (6 mL) and V_{Hep}/V_{Tol} = 0.2 (5.7 mL), showing a similar SR-value. (b) SEM image of well-ordered dot pattern of DS55 annealed at V_{Hep}/V_{Tol} = 0.2 (5.7 mL) for 2 min. A binary solvent induces faster self-assembly speed than pure toluene (5 min).

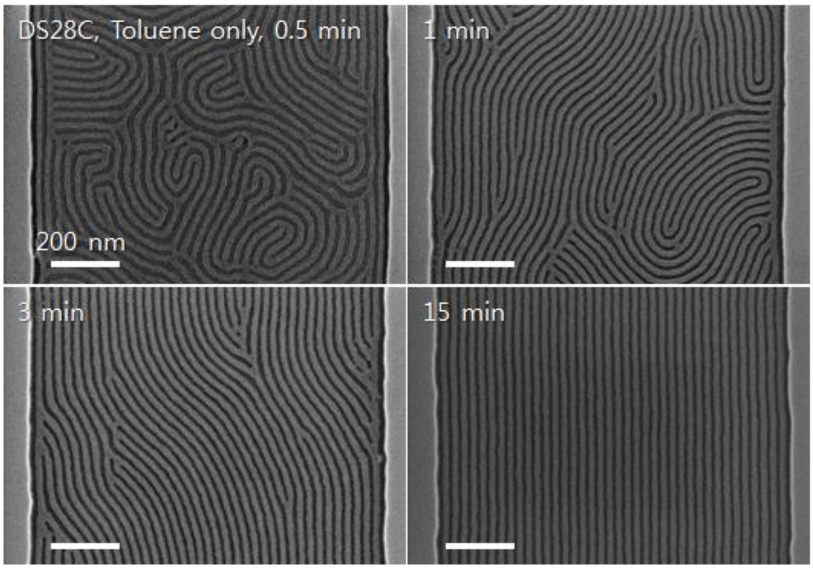

Figure S5. Time-evolution of cylinder-forming DS28C morphology annealed with pure toluene. Well-ordered line pattern was obtained in 15 minutes.

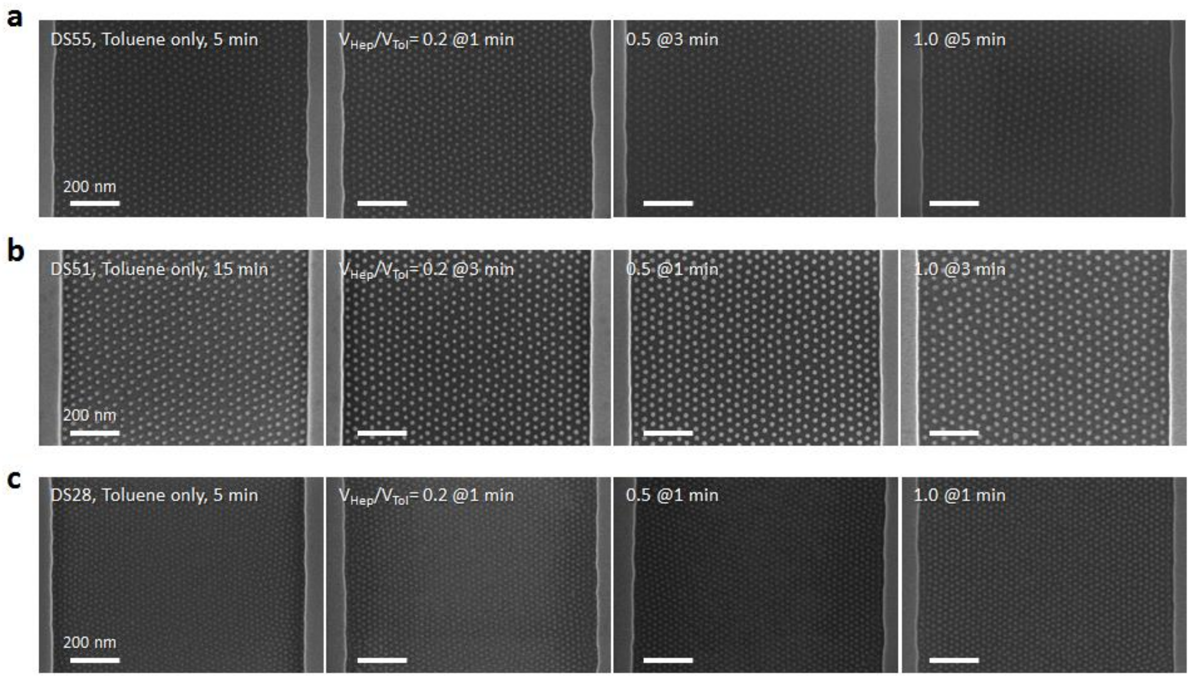

Figure S6. Well-ordered dot patterns of various PDMS-*b*-PS BCPs under the optimum conditions of the toluene and the heptane/toluene mixture. (a-c) Self-assembled morphologies of (a) DS55, (b) DS51, and (c) DS28. SEM images in left column are well-ordered BCP morphologies annealed with pure toluene. Other morphologies are obtained under the optimum annealing conditions (each V_{Hep}/V_{Tol} ratios and annealing time), showing highly ordered dot patterns.

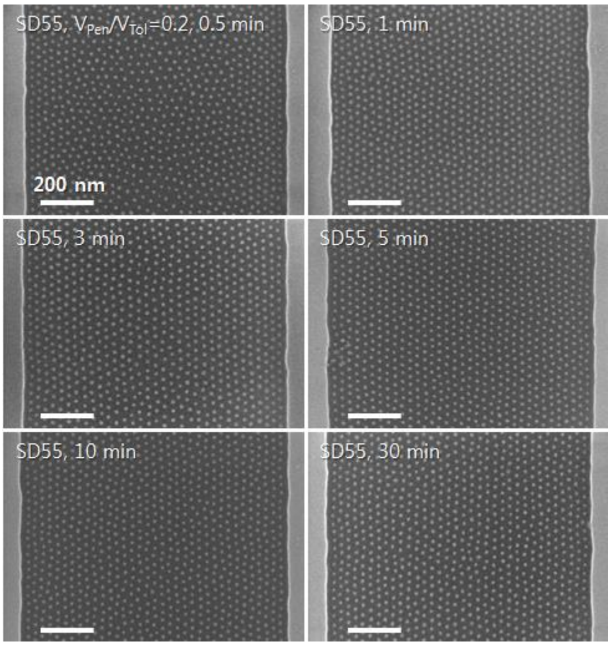

Figure S7. Time-evolution of DS55 morphology annealed when V_{Pen}/V_{Tol} = 0.2. The DS55 BCP was annealed for 0.5 – 30 min, showing well-ordered dot pattern after 1 minute.

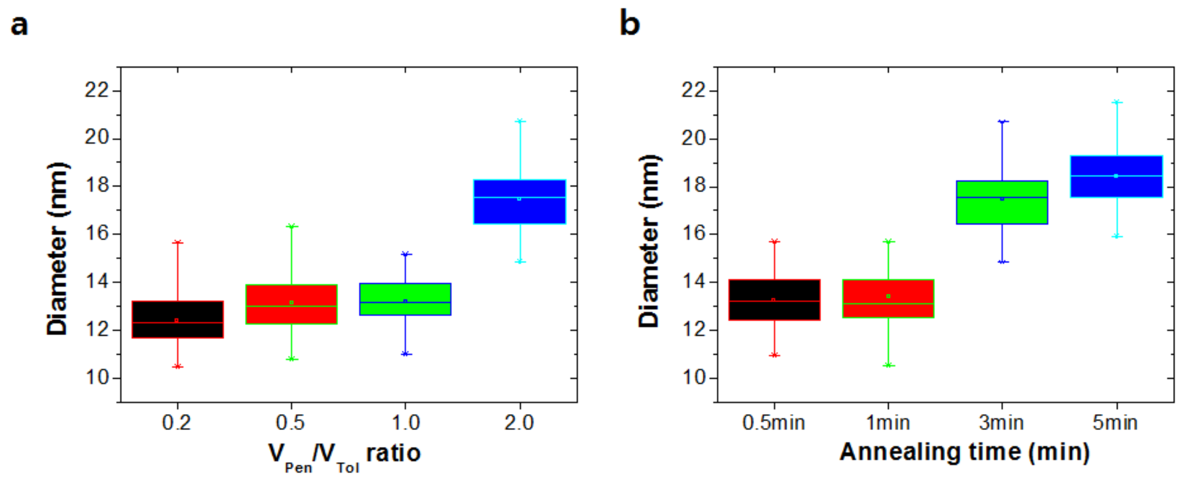

Figure S8. Dot size distribution of DS55 at varied V_{Pen}/V_{Tol} ratio, and annealing time at a fixed V_{Pen}/V_{Tol} ratio of 2.0. Graphs for distribution of diameter vs. (a) V_{Pen}/V_{Tol} and (b) annealing time when V_{Pen}/V_{Tol} = 2.0.