Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supplementary Information

Electric Field Direct Self-Assembly of Block Copolymers for Rapid Formation of Large-Area Complex Nanopatterns

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Supporting discussions

Definition of orientation order parameter and comparison table with relevant researches.

The orientation order parameter indicates the degree of orientation along the principal orientation directions. The general equation is presented below.

$$S = \langle P_2(\cos\theta) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle$$

θ is the angle between the local orientation of patterns and the principal orientation direction (which is the direction of E-field). The brackets denote both temporal and spatial average. This definition is convenient, since for a completely random and isotropic sample, $S = 0$, whereas for a perfectly aligned sample $S = 1$. We present the typical images corresponding to different orientation order parameters (Figure S1) and comparison tables with relevant previous researches (Table S1).

Explanation of relationship between the size of ill-aligned lamellar and diffusion barrier energy.

As the size of ill-aligned grain increased, the total energies getting from the E-field also increased. To lower the entire energies of system, the size of ill-aligned grains should be reduced under the E-field. However, ill-aligned grain will grow until they overcome the inter-block diffusion barrier. In this point of view, blending of low molecular weight components ($SMMA_{10}$), which effectively reduced the inter-block diffusion barrier, stabilize the small sized grain boundary. From the basic formula[1] for E-field DSA as below, the free energy is proportional to the volume of ill-aligned grain. The additional free energy gained from the E-field makes the ill-aligned grain overcomes the diffusion barrier. As a result, the blending of low molecular weight component can stabilize the small size of ill-aligned grain.

$$\Delta F = F_{\parallel} - F_{\perp} = \frac{1}{2}\vec{E}_0^2\epsilon_0(\epsilon - 1)\frac{1-\epsilon}{1+\epsilon}V$$

F :$Free\ energy$
$\vec{E}_0$:$Electric\ field$
ϵ :$Dielectric\ constant$
V :$Volume$

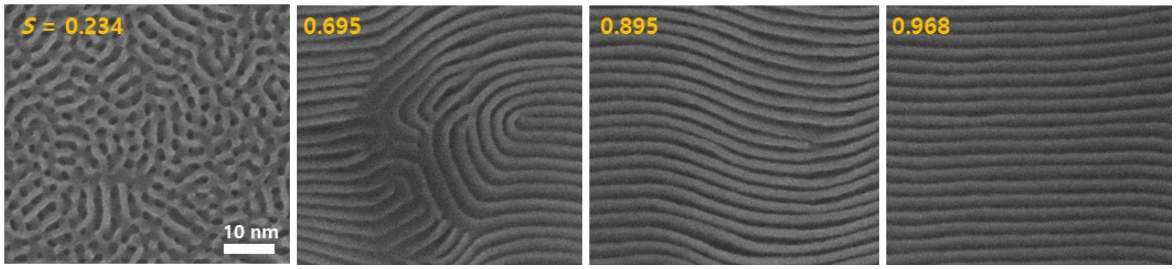


Figure S1. SEM images of SMMA lamellar patterns and corresponding orientation order parameter (*S*) indicates at top of each images.

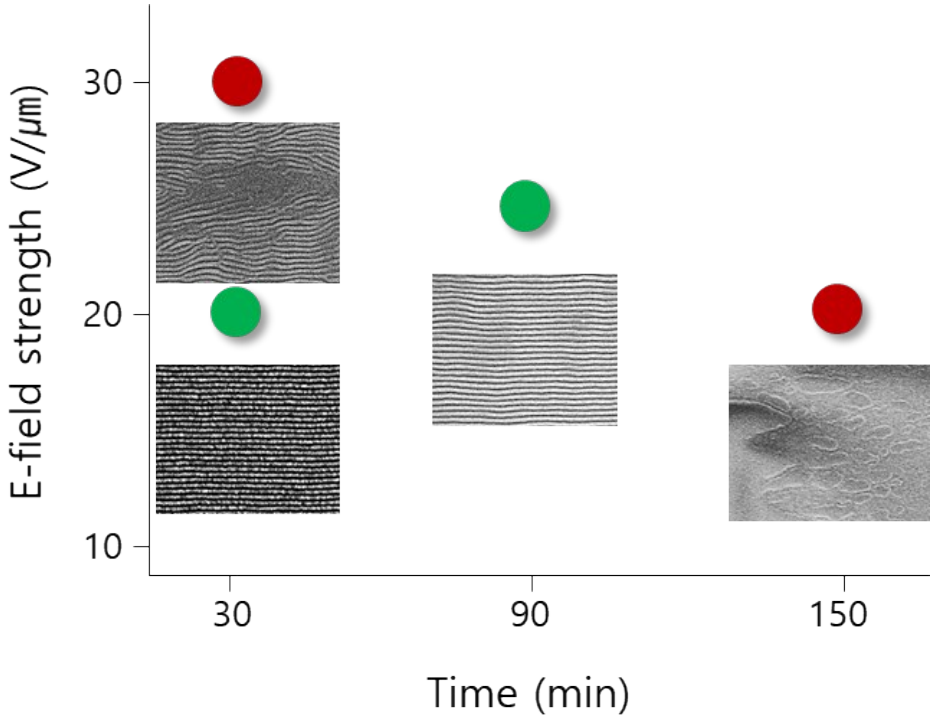


Figure S2. Operation windows for in-plane E-field DSA in this works. Every experiments are conducted on the 240 ℃ hotplate in the air.

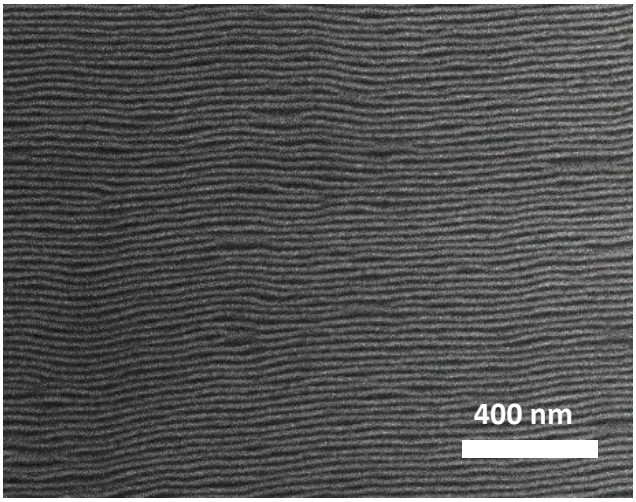


Figure S3. SEM images for 40 wt% $SMMA_{10}$ blended $SMMA_{51}$ thermally annealed for 10 minutes at 240 ℃ under the 25 V/μm.

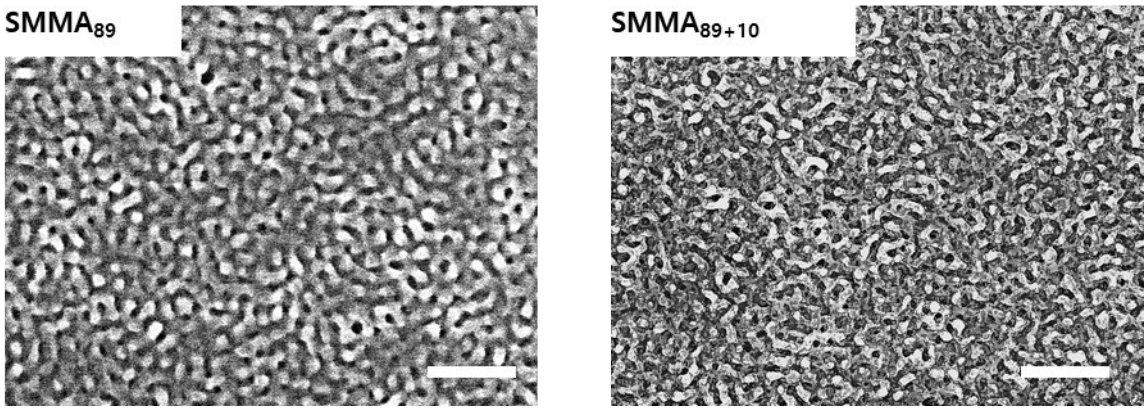


Figure S4. SEM images for as spun thin film of $SMMA_{89}$ and $SMMA_{89+10}$. To enhance the contrast of images, O_2 reactive ion etching process is conducted slightly. White scale bar at the bottom of each images indicate 200 nm.

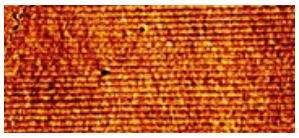
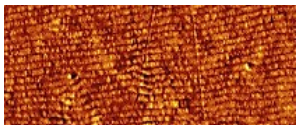
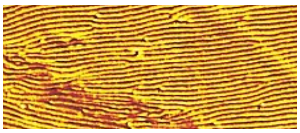
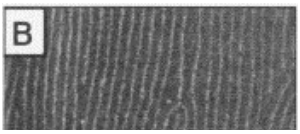
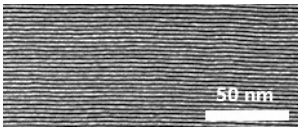
In-Plane DSA Technique	Block copolymers	Processing Condition	Representative Images
E-field DSA[2] (Solvent annealing)	PS-*b*-P2VP 100 kg/mol (Lamellae)	20 hour in Toluene Vapor 15 V/μm	
E-field DSA[3] (Solvent annealing)	PS-*b*-PHEMA-*b*-PMMA 100 kg/mol (Lamellae)	250 min in Toluene Vapor 15 V/μm	
E-field DSA[4] (Solvent annealing)	PS-*b*-P2VP 99 kg/mol w/ Au NP 6 wt% (Lamellae)	90 min in Toluene Vapor 10 V/μm	
E-field DSA[5] (Thermal annealing)	PS-*b*-PMMA 101 kg/mol (Cylinder)	24 hour in Ar at 250 ℃ 3.7 KV/cm	
E-field DSA (Thermal annealing)	PS-*b*-PMMA 51 kg/mol + 10 Kg /mol (Lamellae)	**10 min in Air at 240 ℃ 24 V/μm**	

Table. S1. Comparison table of various in-plane E-field DSA techniques, which shows well aligned structures. Their representative images are shows right side. Our work is presented in bold.

References

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