# Electronic Supplementary Information (ESI)

## Synthesis of poly(styrene-*b*-4-(*tert*-butyldimethylsiloxy)styrene) block copolymers and characterization of their self-assembled patterns

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**Table S1.** Synthesis results of PS-*b*-P4BDSS by anionic polymerization

| sample | s-BuLi[a] | monomer | | block copolymer (homopolymer) $M_n \times 10^{-3}$ | | $M_w/M_n$[d] | domain size[e] | morphology[f] |
|---|---|---|---|---|---|---|---|---|
| | mmol | 1st, mmol | 2nd, mmol | calcd[b] | obsd[c] | | nm | |
| **A-13** | 0.090 | A, 5.99 | B, 1.78 | 11.7 (6.9) | 12.5 (7.5) | 1.01 (1.02) | - | DIS |
| **A-54** | 0.021 | A, 7.48 | B, 1.53 | 53.2 (36.5) | 54.2 (37.1) | 1.05 (1.06) | 38.3 | CYL |
| **A-33** | 0.032 | A, 7.04 | B, 1.41 | 32.3 (22.0) | 33.2 (22.9) | 1.03 (1.04) | 21.5 | CYL |
| **A-25** | 0.015 | A, 6.20 | B, 1.27 | 24.0 (17.1) | 25.3 (16.3) | 1.01 (1.05) | 16.4 | CYL |
| **A-117** | 0.020 | A, 12.0 | B, 2.41 | 93.8 (62.4) | 116.6 (63.0) | 1.06 (1.12) | 54.8 | LAM |
| **A-30** | 0.028 | A, 3.84 | B, 1.95 | 32.6 (14.3) | 29.8 (15.9) | 1.03 (1.01) | 20.3 | LAM |
| **A-27** | 0.041 | A, 7.95 | B, 1.21 | 25.4 (19.1) | 26.8 (19.9) | 1.01 (1.03) | 18.9 | CYL + HPL |

[a] sec-Butyllithium used as initiator of anionic polymerization. [b] *M*n(calcd) = (molecular weight of monomer) × [monomer] / [initiator]. [c] *M*n of the block copolymer was determined by using *M*n of poly(**A**) and the molar ratio of each block estimated by 1H NMR. [d] *M*w/*M*n was determined by using SEC calibration with PS standards in a THF solution containing 2% triethylamine as the eluent at 40 °C. [e] Domain size of BCPs was measured by bulk SAXS. [f] Morphology of BCPs was confirmed by bulk SAXS, where DIS: disorder, CYL: cylinder, LAM: lamellae, and HPL: Hexagonally perforated lamellae.

**Table S2.** Synthesis results of PS-*b*-P4BDSS by RAFT polymerization

| sample | RAFT[a] | AIBN | monomer | | block copolymer (homopolymer) $M_n \times 10^{-3}$ | $M_w/M_n$[d] | domain size[e] | morphology[f] |
|---|---|---|---|---|---|---|---|---|
| | Mmol | Mmol | 1st, mmol | 2nd, mmol | obsd[c] | | nm | |
| **R-55** | 0.021 | 0.011 | A, 3.62 | B, 2.30 | 55.1 (36.3) | 1.14 (1.21) | -39.2 | CYL |
| **R-54** | 0.021 | 0.011 | A, 3.62 | B, 2.33 | 54.3 (36.3) | 1.32 (1.21) | 39.2 | CYL |
| **R-25** | 0.020 | 0.010 | A, 1.64 | B, 1.13 | 25.2 (16.2) | 1.15 (1.17) | 16.5 | CYL |
| **R-26** | 0.020 | 0.010 | A, 1.64 | B, .1.15 | 25.7 (16.2) | 1.21 (1.17) | 16.8 | CYL |

[a] sec-Butyllithium used as initiator of anionic polymerization. [b] $M_n$ of the block copolymer was determined by using $M_n$ of poly(**A**) and the molar ratio of each block estimated by 1H NMR. [c] $M_w/M_n$ was determined by using SEC calibration with PS standards in a THF solution containing 2% triethylamine as the eluent at 40 °C. [d] Domain size of BCPs was measured by bulk SAXS. [e] Morphology of BCPs was confirmed by bulk SAXS, where DIS: disorder, CYL: cylinder, LAM: lamellae, and HPL: Hexagonally perforated lamellae.

**Table S3.** Pattern quality comparison between various BCPs with different χ.

| | CD (nm) | χ | PDI | LER (nm) | LWR (nm) | Annealing Methods |
|---|---|---|---|---|---|---|
| PS-*b*-PMMA[a] | 10.5[d] | 0.0324 | 1.06 | 4.85±0.71 | - | Thermal Annealing |
| PS-*b*-P4BDSS | 11.4 | 0.0525 | 1.01 | 3.25±0.54 | 3.02±0.28 | Thermal Annealing |
| | 18.4 | | 1.14 | 3.41±0.85 | 2.85±0.48 | Thermal Annealing |
| PS-*b*-PDMS[b] | 13.6 | 0.0950 | 1.09 | 4.83±0.19 | 4.11±0.23 | Solvent Annealing |
| | 13.3 | | | 2.85±0.12 | 2.54±0.16 | Solvothermal Annealing |
| P4VP-*b*-PDMS[c] | 17.6 | 0.6650 | 1.25 | 1.88±0.17 | 0.98±0.07 | Solvothermal Annealing |

[a] According to K. S. Lee *et al*, *ACS Applied Materials & Interfaces*, 2017. **9**. 31245-31251. [b] According to J. M. Kim *et al*, *Advanced Functional Materials*, 2015, **25**, 306-315. [c] According to J. M. Kim *et al*, *Chemistry of Materials*, 2016, **28**, 5680-5688. [d] CD of PS-*b*-PMMA was calculated by half of domain size.

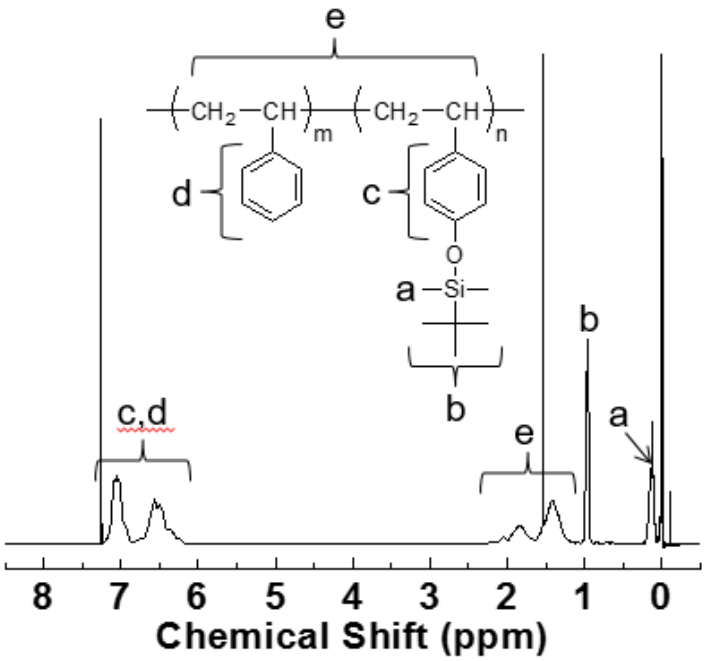


**Figure S1.** Characteristics of $^{1}$H NMR of PS-*b*-P4BDSS

According to **Leibler's mean-field theory,**

$I(q) = K[S(q) / W(q) - 2\chi]^{-1}$

where K is a proportionality constant which is not important in the present work and is defined in the text.

$S(q) = \langle S_{x,x}(q) \rangle_v + 2\langle S_{x,y}(q) \rangle_v + \langle S_{y,y}(q) \rangle_v$

$W(q) = \langle S_{x,x}(q) \rangle_v * \langle S_{y,y}(q) \rangle_v - \langle S_{y,y}(q) \rangle_v^2$

where,

$\langle S_{x,x}(q) \rangle_v = r_{c,n} f_{x,n}^2 g_{x,n}^{(2)}(q)$

$\langle S_{x,y}(q) \rangle_v = r_{c,n} f_x f_y g_{x,n}^{(1)}(q) g_{y,n}^{(1)}(q)$

$r_{c,n} = (v_x N_{x,n} + v_y N_{y,n}) / (v_x * v_y)^{1/2}$

$g_{x,n}^{(1)}(q) = 1/x_{x,n} \{1-[x_{x,n} (\lambda_x-1) + 1]^{-(\lambda x-1)^{-1}}\}$

$g_{x,n}^{(2)}(q) = 1/x_{x,n}^2 \{-1 + [x_{x,n} (\lambda_x-1)+1]^{-(\lambda x-1)^{-1}}\}$

$x_{x,n} = (N_{x,n} b_x^2 / 6) q^2$

$\lambda_{x,n} = N_{x,w} / N_{x,n}$

$v_x$ is molecular volume of X (cm3/mol). $f_X$ is the volume fraction of X. $N_{x,n}$ and $N_{x,w}$ is the number-average and weight-average degree of polymerization of X block chain. $b_X$ is the segment length of X.

**Figure S2.** Calculation of chi in PS-*b*-P4BDSS

| | w (weight fraction) | f (volume fraction) | N (repeating unit) | b (segment length) | v (molar volume) | λ (PDI) |
|---|---|---|---|---|---|---|
| **PS** | 0.600 | 0.634 | 72.0 | 0.57 | 98.6 | 1.03 |
| **P4BDSS** | 0.400 | 0.366 | 21.3 | 0.47 | 194 | 1.10 |

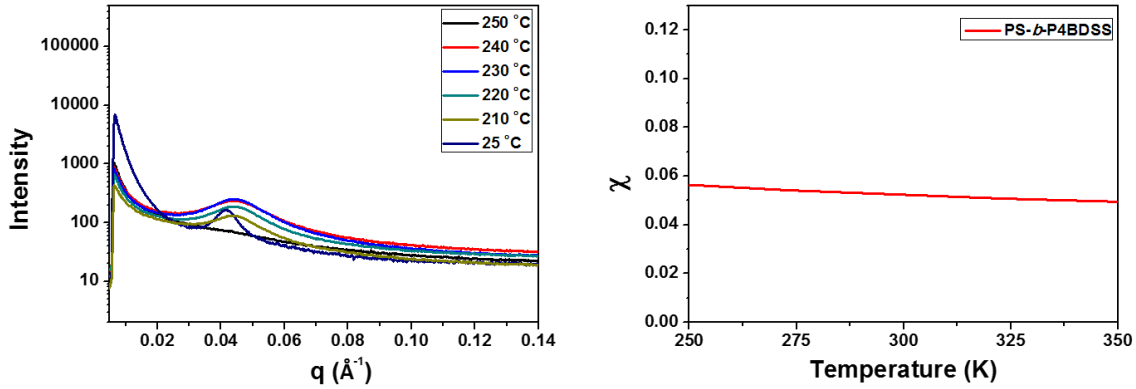


**Figure S3.** Calculation of χ in poly PS-*b*-P4BDSS

| | w (weight fraction) | f (volume fraction) | N (repeating unit) | b (segment length) | v (molar volume) | λ (PDI) |
|---|---|---|---|---|---|---|
| **PMMA** | 0.500 | 0.468 | 179.78 | 0.488 | 84.84 | 1.54 |
| **PS** | 0.500 | 0.532 | 172.83 | 0.681 | 100.14 | 1.18 |

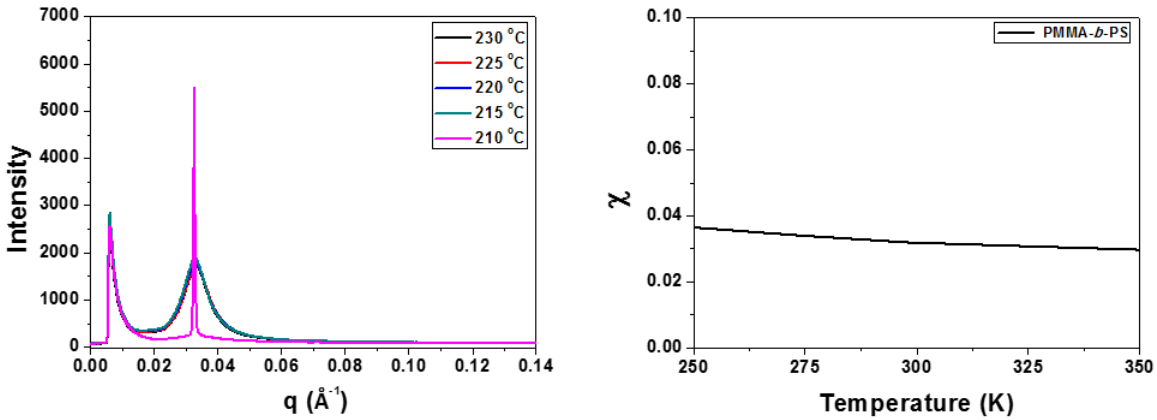


**Figure S4.** Calculation of χ in PS-*b*-PMMA (34k)

| | w (weight fraction) | f (volume fraction) | N (repeating unit) | b (segment length) | v (molar volume) | λ (PDI) |
|---|---|---|---|---|---|---|
| **PDMS** | 0.487 | 0.319 | 31.02 | 0.712 | 104.14 | 1.13 |
| **PS** | 0.513 | 0.681 | 50.12 | 0.681 | 138.50 | 1.76 |

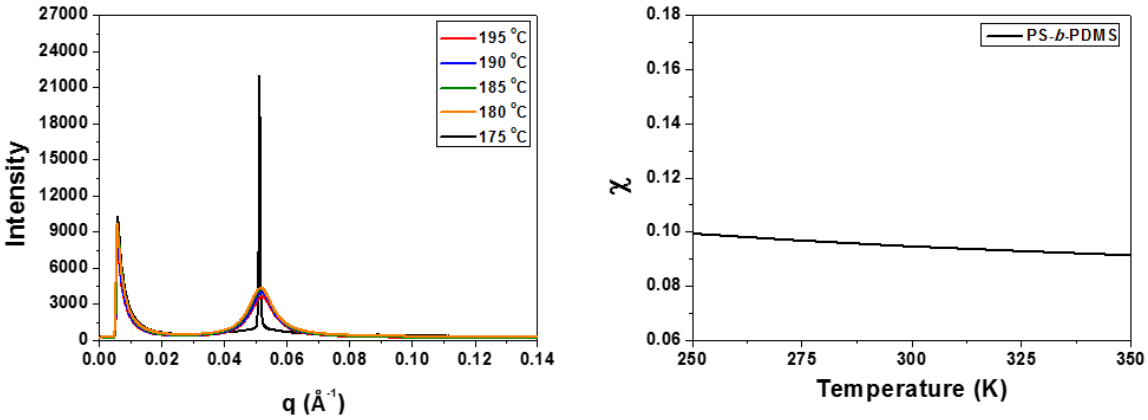


**Figure S5.** Calculation of $\chi$ in PS-*b*-PDMS

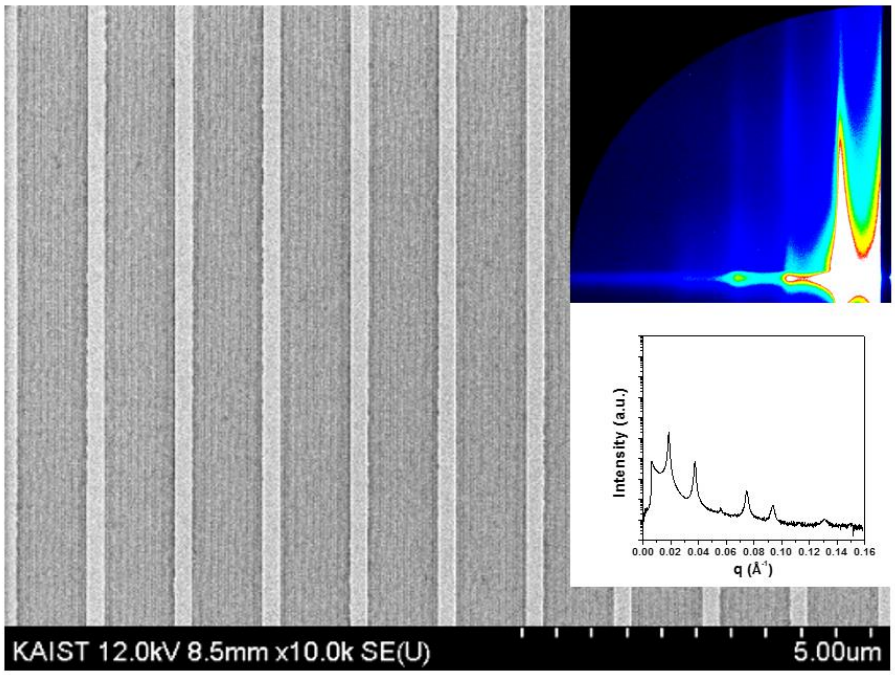


**Figure S6.** SEM and GISAXS measurements of A-54

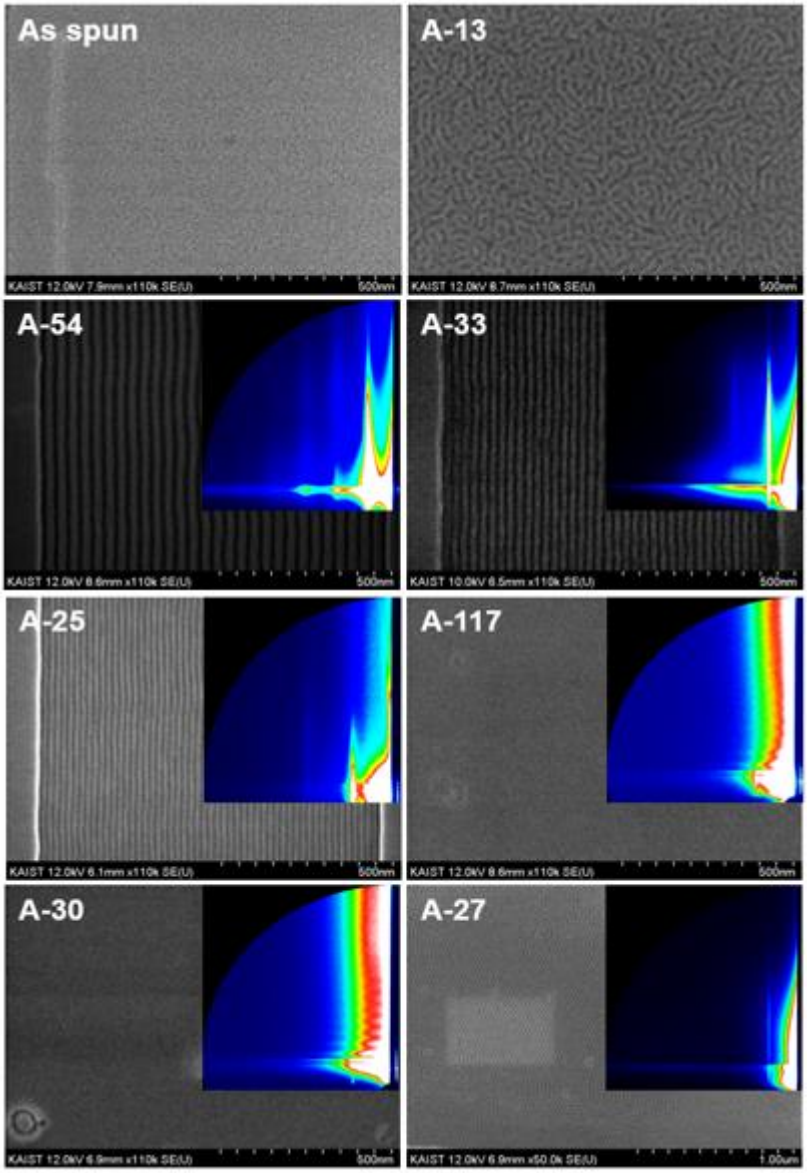


**Figure S7.** Self-assembly of PS-*b*-P4BDSS at 200 °C for 1h.

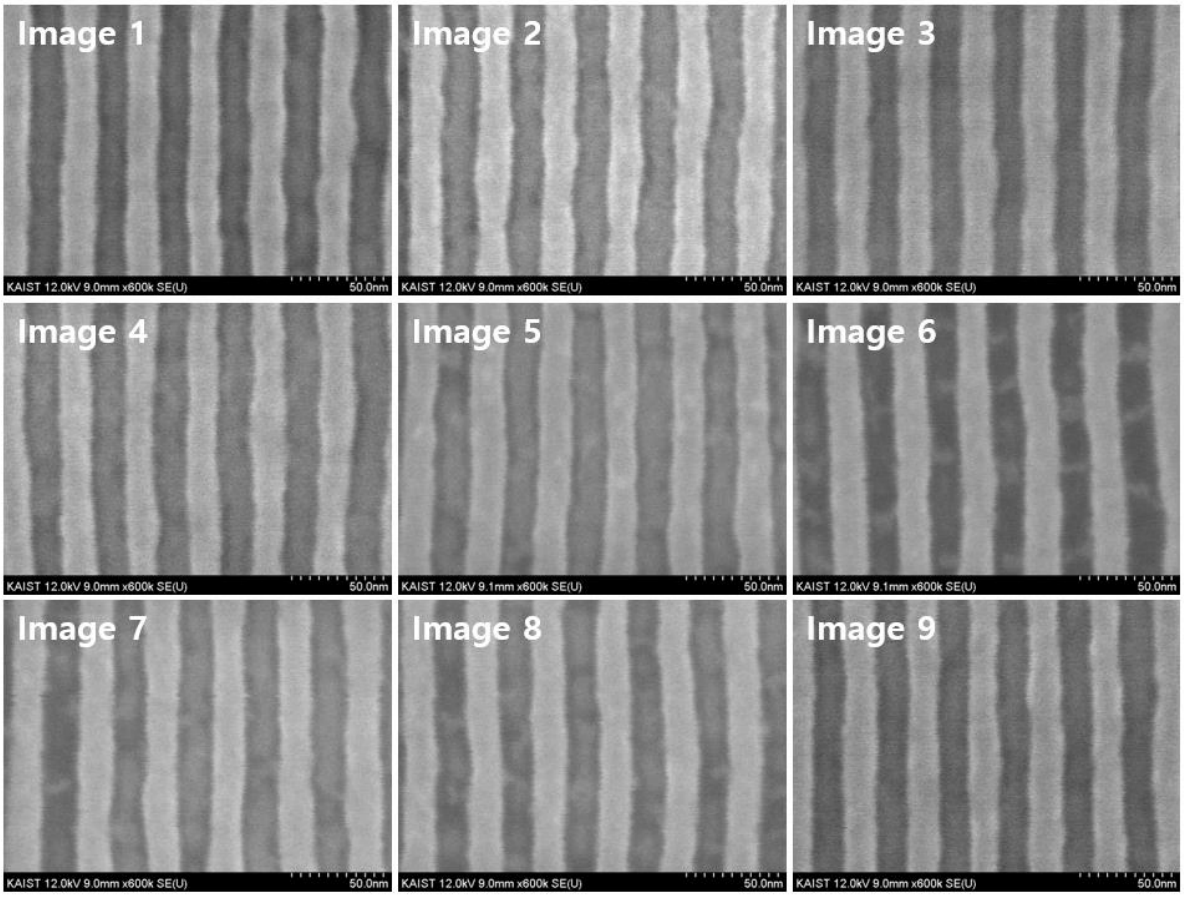


**Figure S8.** Pattern quality analysis of A-54

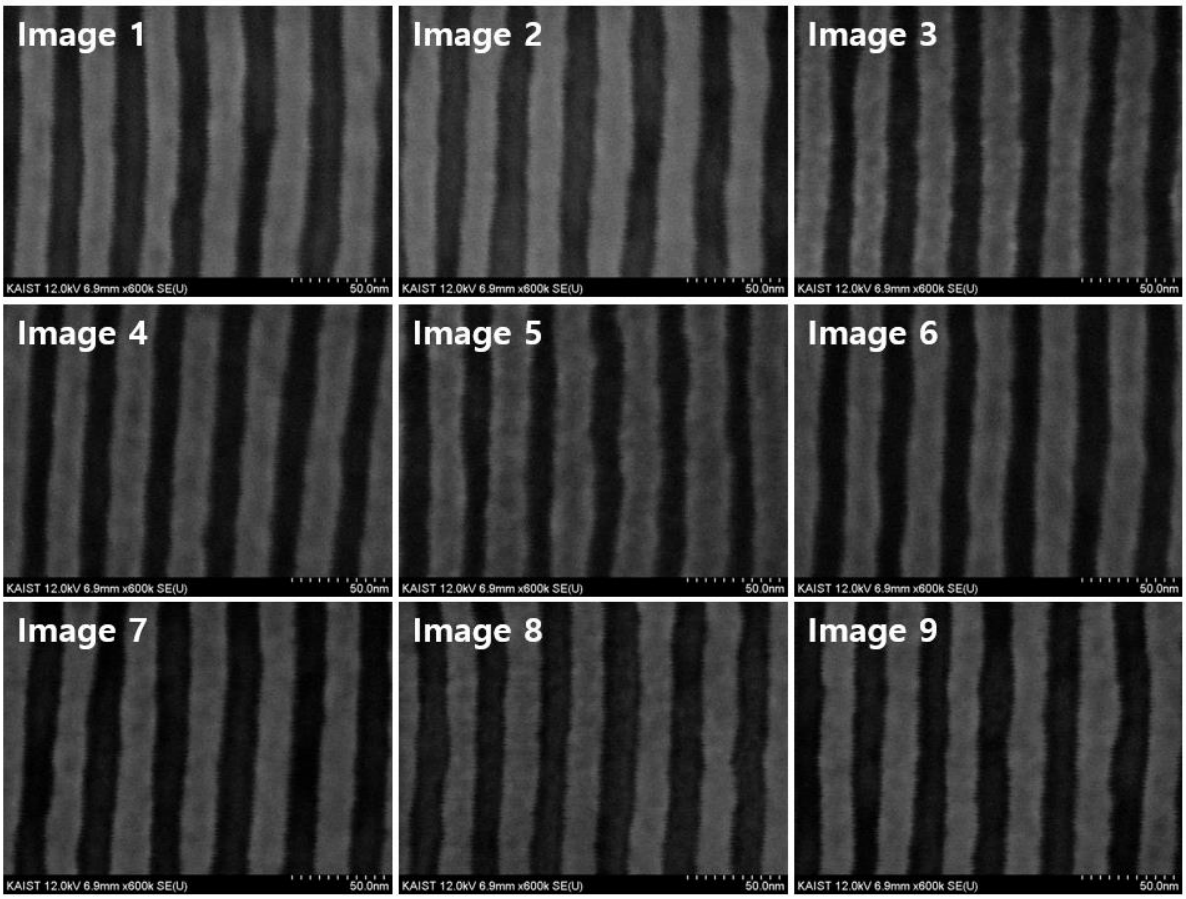


**Figure S9.** Pattern quality analysis of R-55

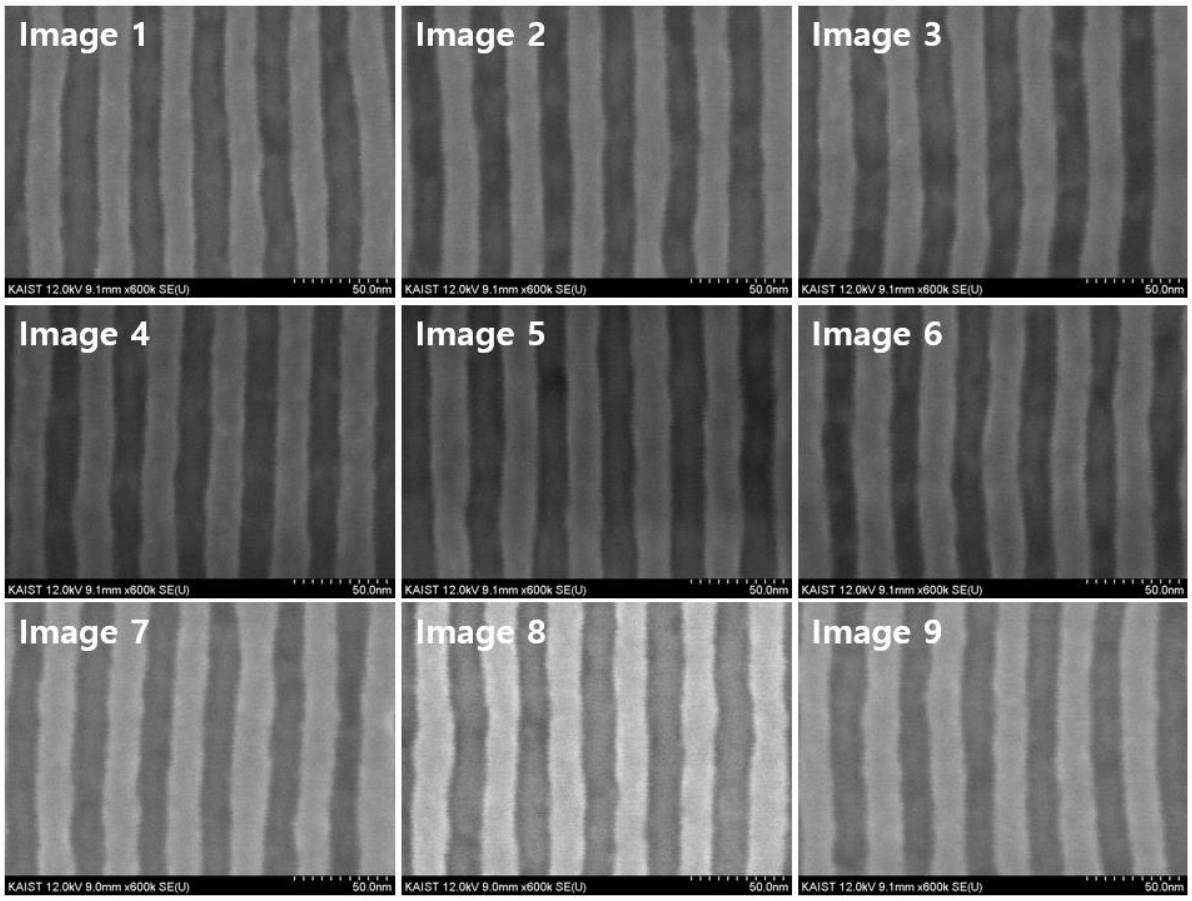


**Figure S10.** Pattern quality analysis of R-54

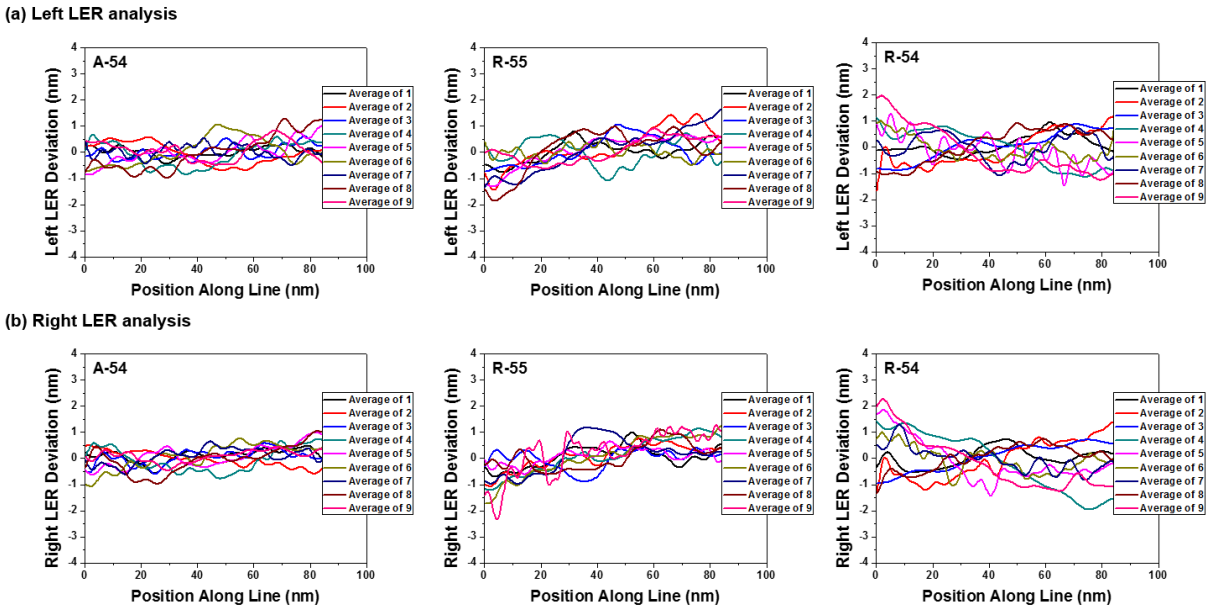


**Figure S11.** LER comparison of PS-*b*-P4BDSS

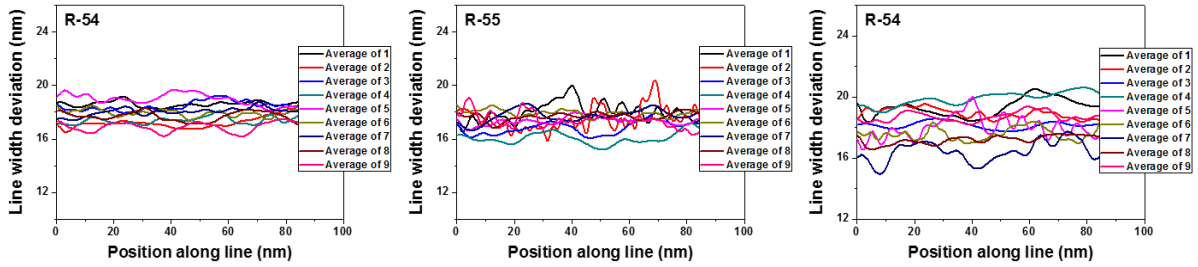


**Figure S12.** LWR comparison of PS-*b*-P4BDSS

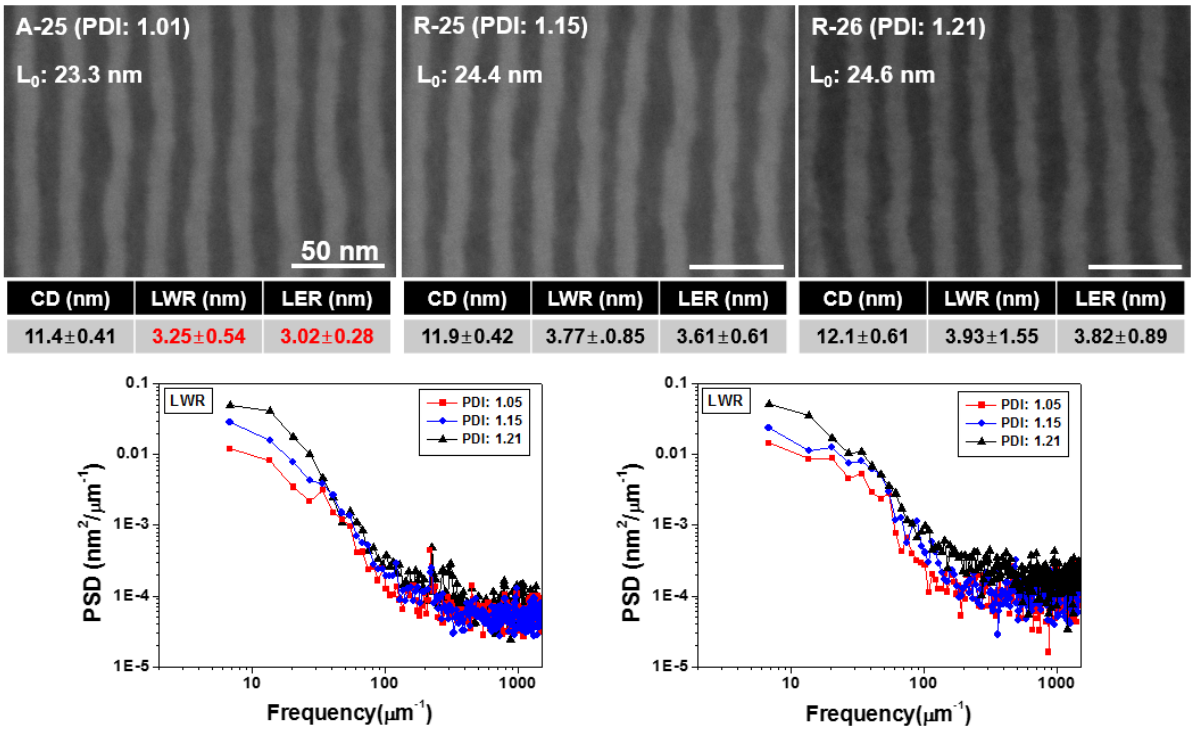


**Figure S13.** Pattern quality comparison of PS-*b*-P4BDSS by changing PDI

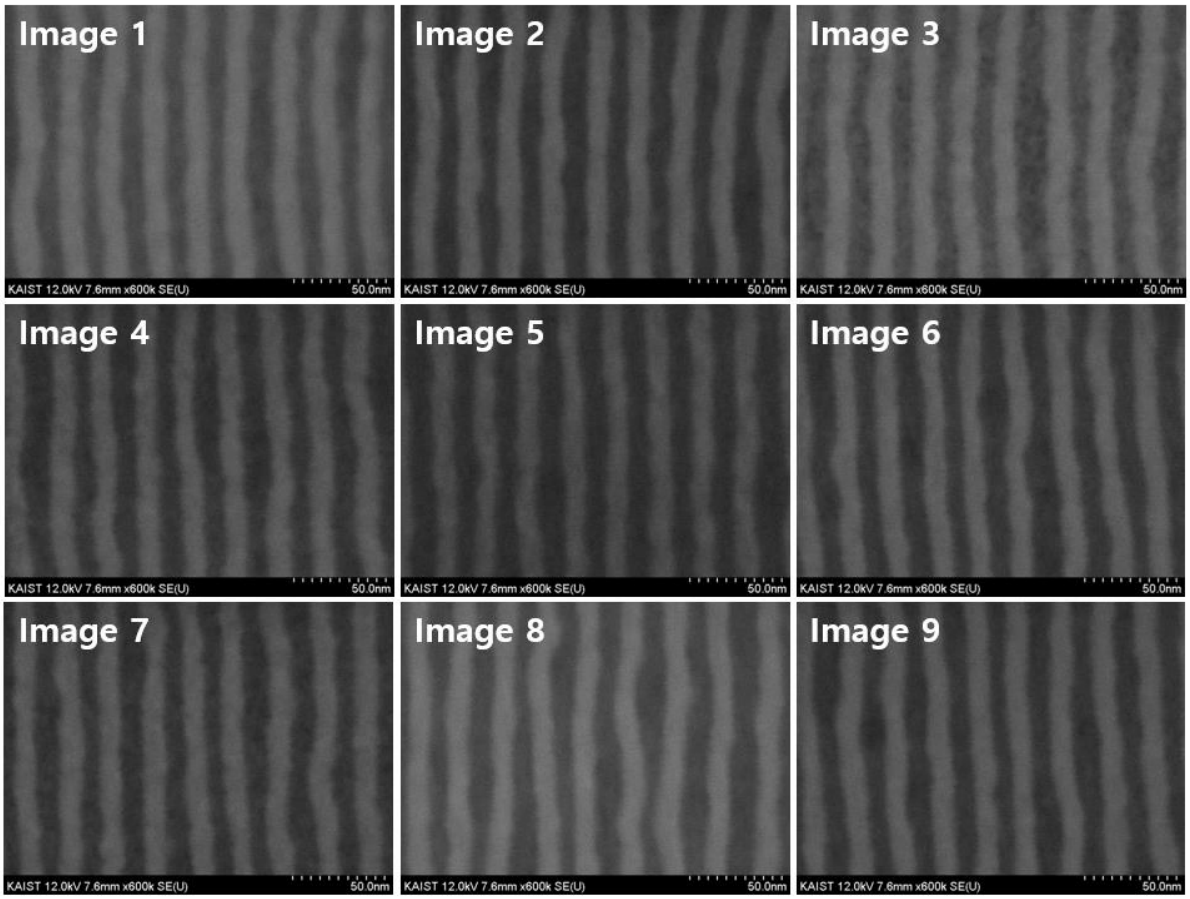


**Figure S14.** Pattern quality analysis of A-25

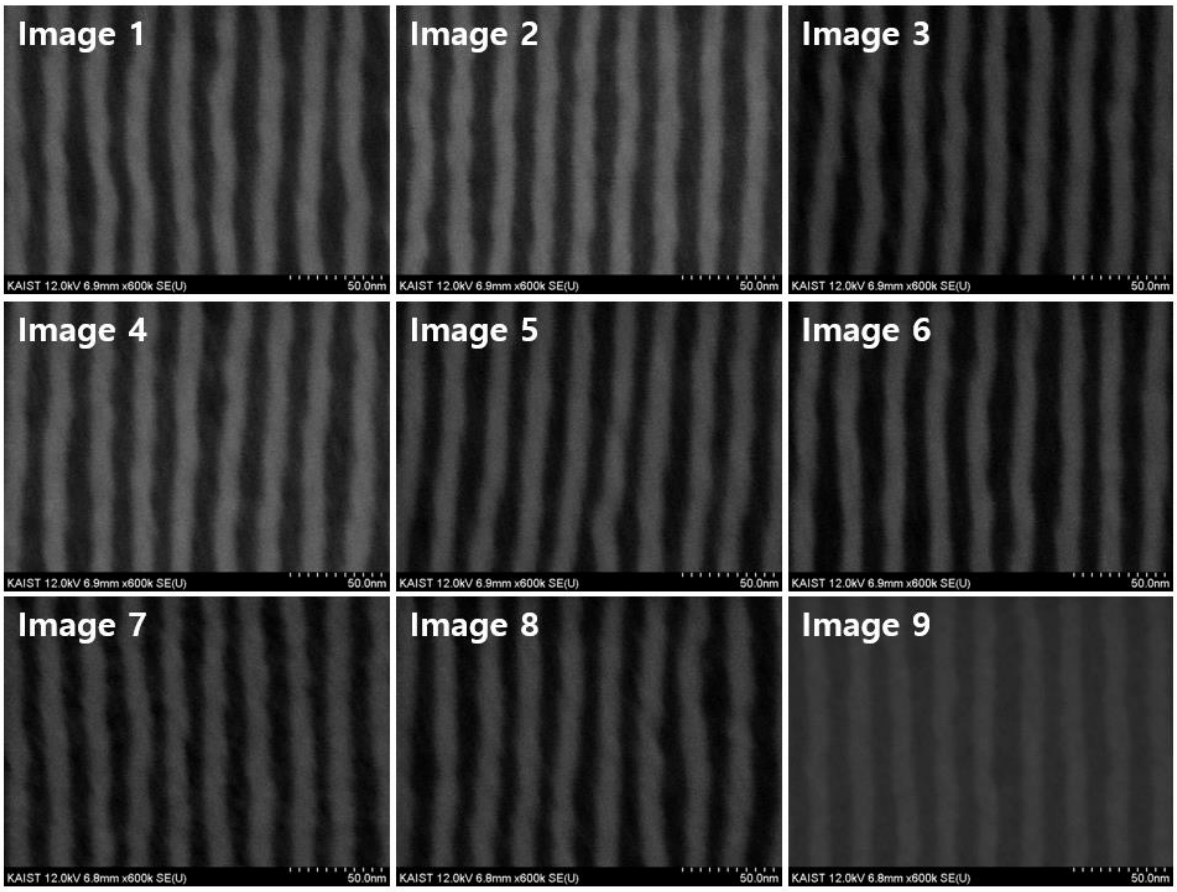


**Figure S15.** Pattern quality analysis of R-25

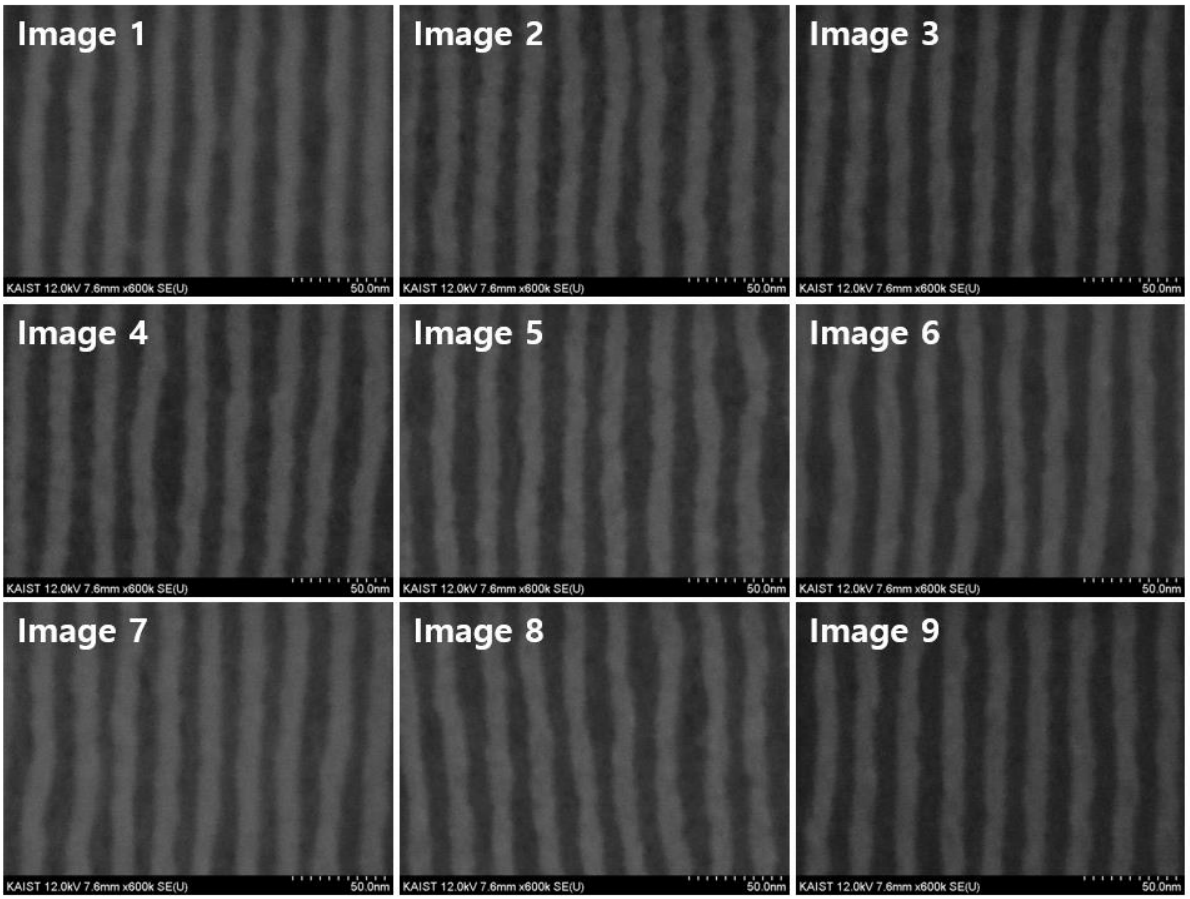


**Figure S16.** Pattern quality analysis of R-26

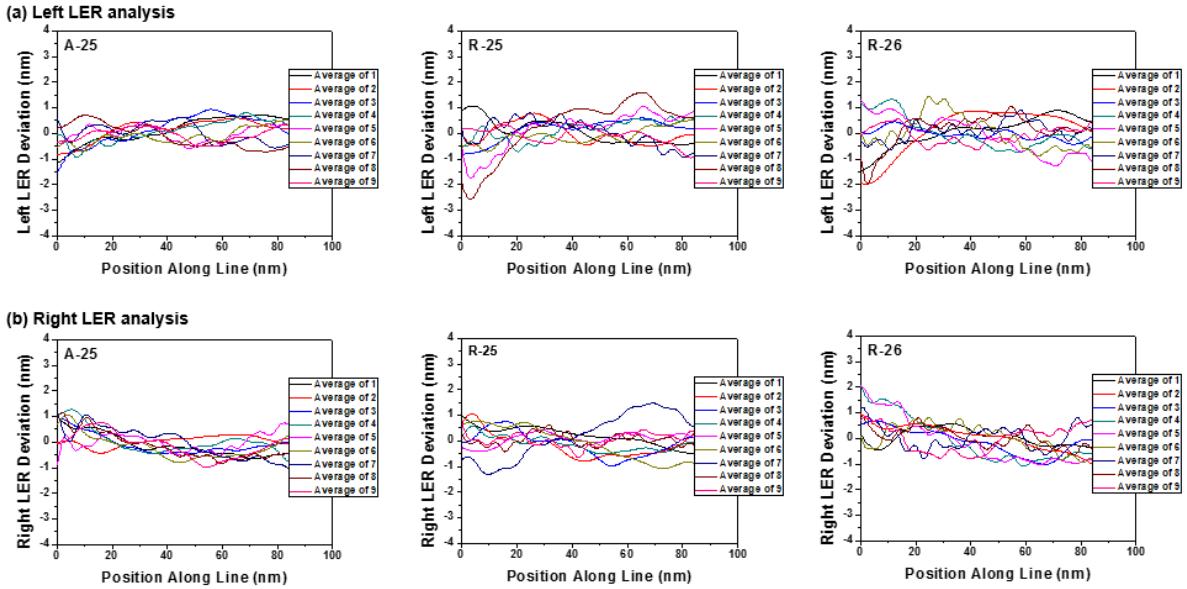


**Figure S17.** LER comparison of PS-*b*-P4BDSS

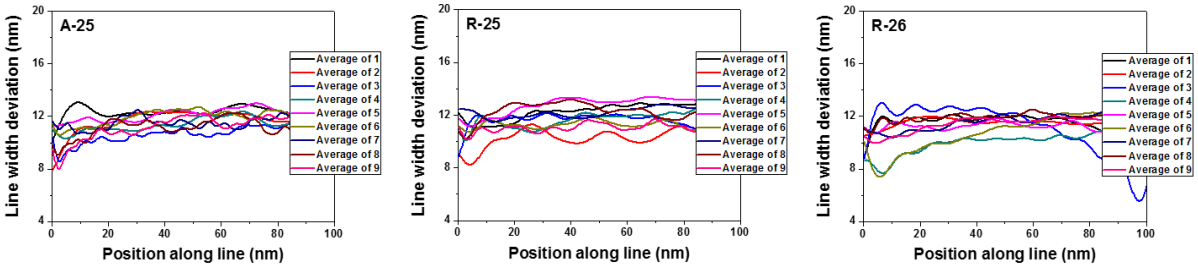


**Figure S18.** LWR comparison of PS-*b*-P4BDSS