

Supplementary Information

Universal vertical standing of block copolymer microdomains enabled by a gradient block

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Thermodynamic calculations: Thermodynamic calculations were demonstrated by the free energy difference of the vertical and symmetric/asymmetric horizontal lamellar phase (F_{ver} , F_{sym} , and F_{asym}) divided by the free energy of bulk BCP (F_0), which is given as:¹

$$\frac{F_{ver}}{F_0} = \frac{1}{3} \left[3 + \frac{1}{d} \left(\frac{\gamma_{air}^{ver} + \gamma_{air}^{ver}}{\gamma_{BCP}} \right) \right] \quad (1)$$

$$\frac{F_{sym}}{F_0} = \frac{1}{3} \left[\left(\frac{d}{n} \right)^2 + \frac{2n}{d} + \frac{1}{d} \left(\frac{\gamma_{sub}^{sym} + \gamma_{sub}^{sym}}{\gamma_{BCP}} \right) \right] \quad (2)$$

$$\frac{F_{asym}}{F_0} = \frac{1}{3} \left[\left(\frac{d}{n + \frac{1}{2}} \right)^2 + \frac{2 \left(n + \frac{1}{2} \right)}{d} + \frac{1}{d} \left(\frac{\gamma_{air}^{asym} + \gamma_{sub}^{asym}}{\gamma_{BCP}} \right) \right] \quad (3)$$

$$\gamma_{BCP} = \left(\frac{\chi}{6} \right)^{\frac{1}{2}} \frac{k_B T}{b^2} \quad (4)$$

where γ_{BCP} is the interfacial energy of the block copolymer, γ_{air} is the surface energy of the each film, γ_{sub} is the interfacial energy between the substrate and the BCP film, d is the thickness of the BCP film (unit of bulk periodicity L_0), n is an integer, k_B is the Boltzman constant, and b is the segment length.

To calculate $\Delta\gamma_{Bot}$, the interfacial energy of the bulk polymer ($\gamma_{AB}^{(Bulk)}$) was calculated based on the following equation:

$$\gamma_{AB}^{(Bulk)} = \chi \cdot \frac{k_B T}{b^2} \quad (5).$$

¹ Durand, W. J.; Carlson, M. C.; Maher, M. J.; Blachut, G.; Santos, L. J.; Tein, S.; Ganesan, V.; Ellison, C. J.; Willson, C. G. Experimental and modeling study of domain orientation in confined block copolymer thin films. *Macromolecules* **2015**, *49*, 308-316.

Measurement of Flory-Huggins interaction parameter (χ) of the block copolymer: Using bulk SAXS measurement, the intensity dependence with temperature can be obtained. At a higher temperature than the order-disorder temperature, the polymer has become a disordered phase. In the Leibler's mean field theory, the intensity of the SAXS measurement $I(q)$ has the relationship delineated below:²

$$I(q) = K' \left[\frac{\bar{S}(q)}{\bar{W}(q)} - 2\chi \right]^{-1} \quad (6)$$

where K' is a proportionality constant and $\bar{S}(q)$ and $\bar{W}(q)$ are defined as:

$$\bar{S}(q) = \langle S_{AA}(q) \rangle_v + 2 \langle S_{AB}(q) \rangle_v + \langle S_{BB}(q) \rangle_v \quad (7)$$

$$\bar{W}(q) = \langle S_{AA}(q) \rangle_v \langle S_{BB}(q) \rangle_v - \langle S_{AB}(q) \rangle_v^2 \quad (8)$$

$$\langle S_{AA}(q) \rangle_v = r_{c,n} f_{A,n}^2 g_{A,n}^{(2)}(q) \quad (9)$$

$$\langle S_{BB}(q) \rangle_v = r_{c,n} f_{B,n}^2 g_{B,n}^{(2)}(q) \quad (10)$$

$$\langle S_{AB}(q) \rangle_v = r_{c,n} f_{A,n} f_{B,n} g_{A,n}^{(1)}(q) g_{B,n}^{(1)}(q) \quad (11)$$

$$r_{c,n} = \left(\frac{v_A}{v_0} \right) N_{A,n} + \left(\frac{v_B}{v_0} \right) N_{B,n} \quad (12)$$

where $v_0 = (v_A v_B)^{1/2}$ (v_K : molar volume of the K th monomer).

$$f_{K,n} = N_{K,n} v_k / (N_{A,n} v_a + N_{B,n} v_B) \quad (13)$$

where $N_{K,n}$: number-average degree of polymerization

² Leibler, L. Theory of Microphase Separation in Block Co-Polymers. *Macromolecules* **1980**, *13*, 1602-1617.

$$g_{K,n}^{(1)}(q) = \frac{1}{x_{K,n}} \{1 - [x_{K,n}(\lambda_K - 1) + 1]^{-(\lambda_K - 1)^{-1}}\} \quad (14)$$

$$g_{K,n}^{(2)}(q) = \frac{1}{x_{K,n}^2} \{-1 + x_{K,n} [x_{K,n}(\lambda_K - 1) + 1]^{-(\lambda_K - 1)^{-1}}\} \quad (15)$$

where $x_{K,n} \equiv \left(\frac{N_{K,n} b_K^2}{6}\right) q^2$ (b_K : segment length of K), $\lambda_K = N_{K,W}/N_{K,n}$

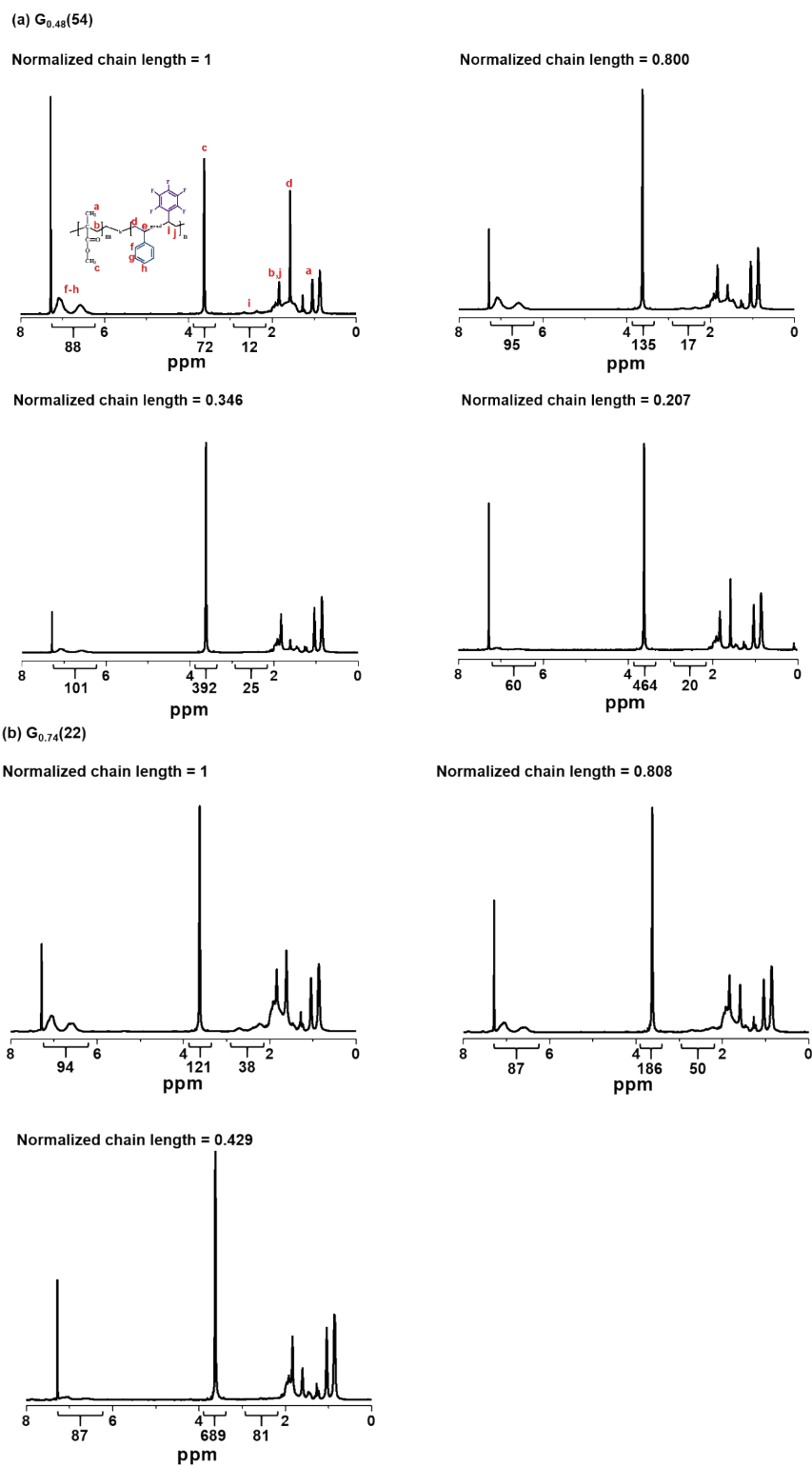
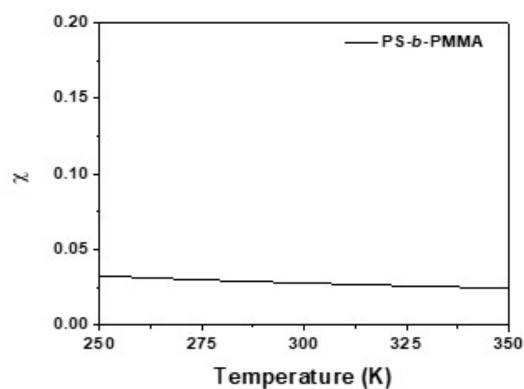
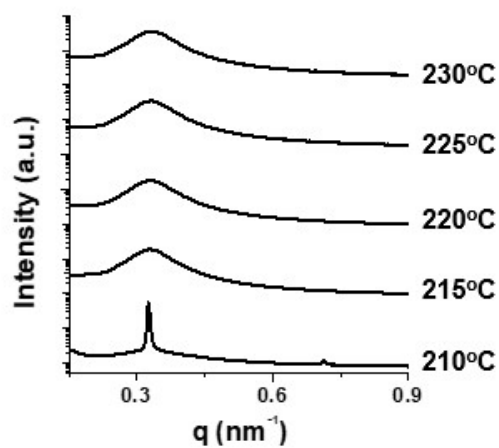


Fig. S1. NMR results of the block copolymers with gradient random-copolymer blocks.

(a) $G_{0.48}(54)$, and (b) $G_{0.74}(22)$ with different chain length. Integration of the intensity of each peak (PS [5H], PMMA [3H], and PPFs [2H]) are provided below.

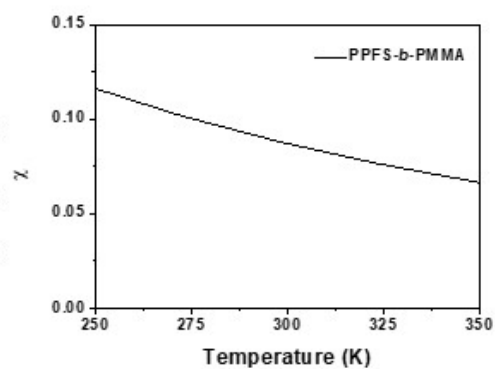
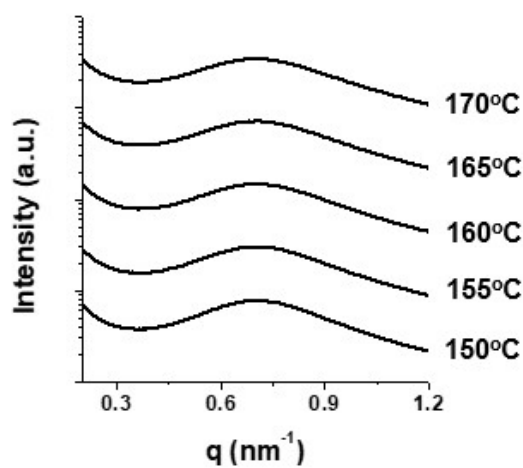
(a)

	w (weight fraction)	f (volume fraction)	N (repeating unit)	b (segment length)	v (molar volume)	λ (PDI)
PMMA	0.500	0.468	180	0.488	84.84	1.54
PS	0.500	0.532	173	0.681	100.14	1.18



(b)

	w (weight fraction)	f (volume fraction)	N (repeating unit)	b (segment length)	v (molar volume)	λ (PDI)
PPFS	0.568	0.313	20	0.568	137.3	1.33
PMMA	0.432	0.687	71	0.539	84.84	1.13



(c)

	w (weight fraction)	f (volume fraction)	N (repeating unit)	b (segment length)	v (molar volume)	Λ (PDI)
P(S-g-PFS)	0.699	0.579	93	0.561	125.02	1.25
PMMA	0.301	0.421	66	0.539	84.84	1.1

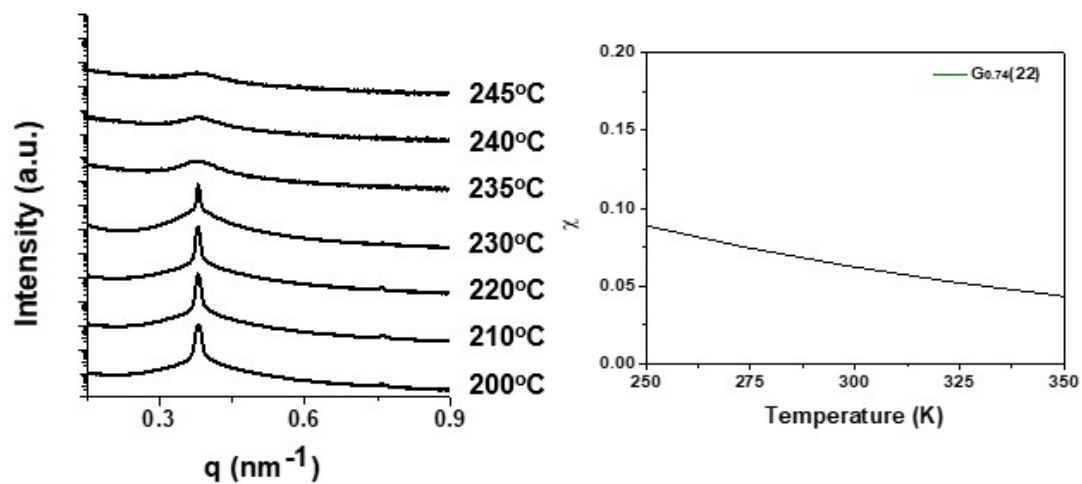
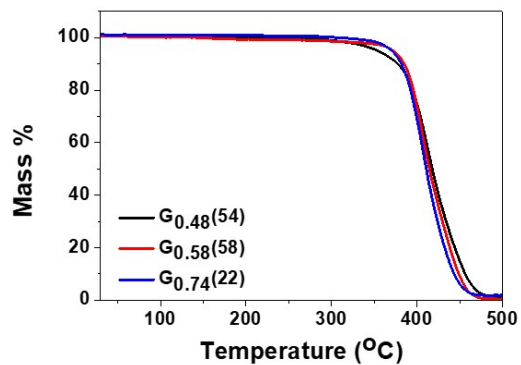


Fig. S2. Bulk small angle X-ray scattering analysis of the block copolymers. Measurement of χ value by SAXS with increasing temperature of (a) PS-*b*-PMMA, (b) PPFS-*b*-PMMA, and (c) $G_{0.74}(22)$

(a)



(b)

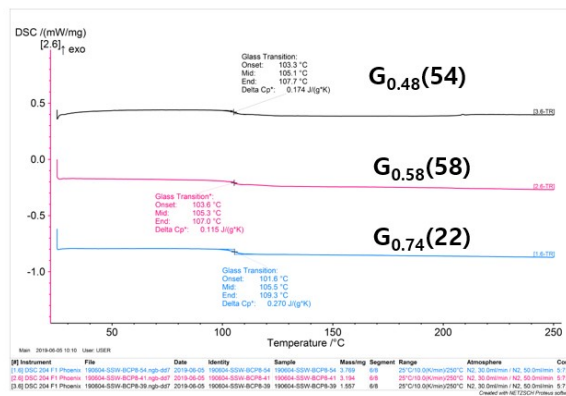


Fig. S3. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) data of GRC-BCPs

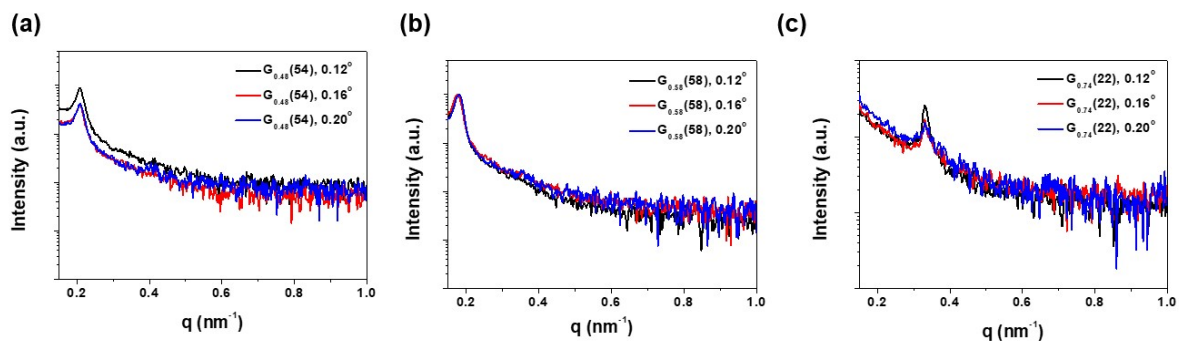


Fig. S4. GISAXS analysis data with different incidence angles (a) $G_{0.48}(54)$, (b) $G_{0.58}(58)$, and (c), $G_{0.74}(22)$.

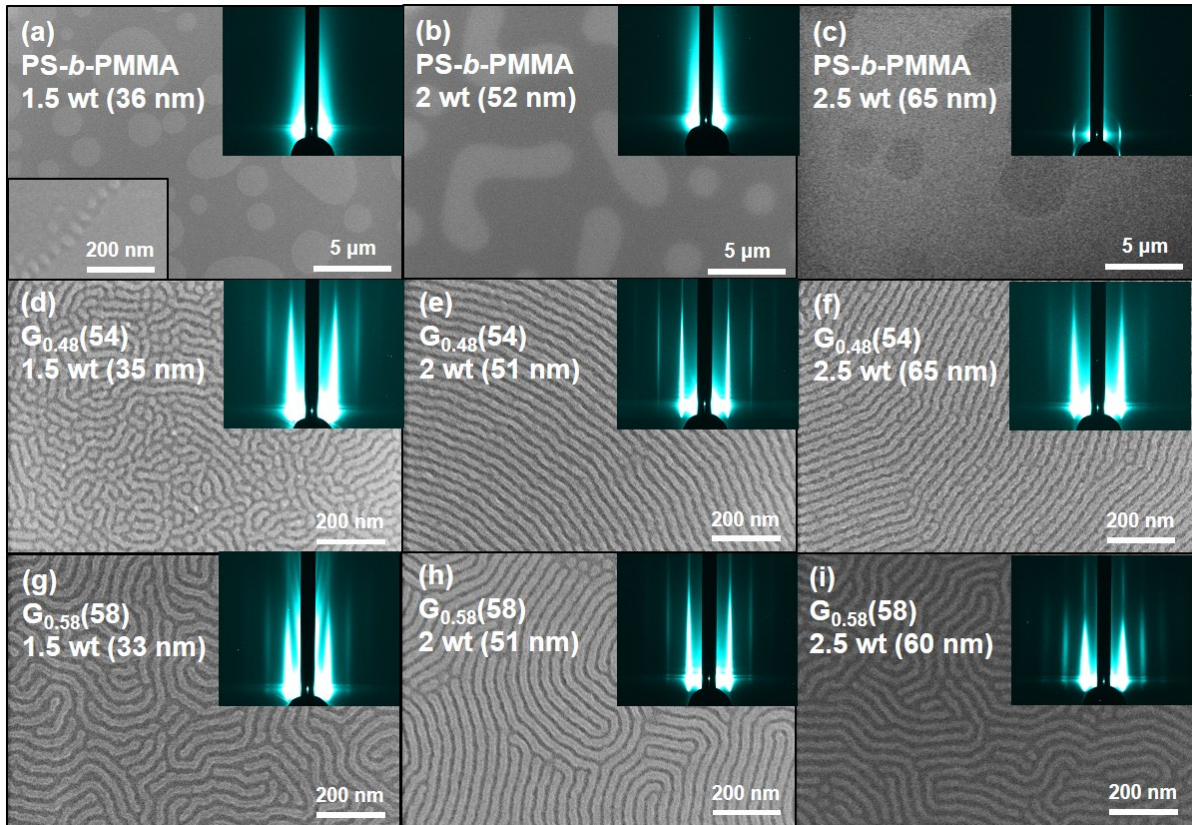


Fig. S5. Self-assembly of the block copolymers above silicon with native oxide substrate with PS-*b*-PMMA ((a)-(c)), $G_{0.48}(54)$ ((d)-(f)), and $G_{0.58}(58)$ ((g)-(i)) with different thickness (1.5~2.5 wt% in PGMEA solution). Each BCP was annealed at 300 °C, 10 min.

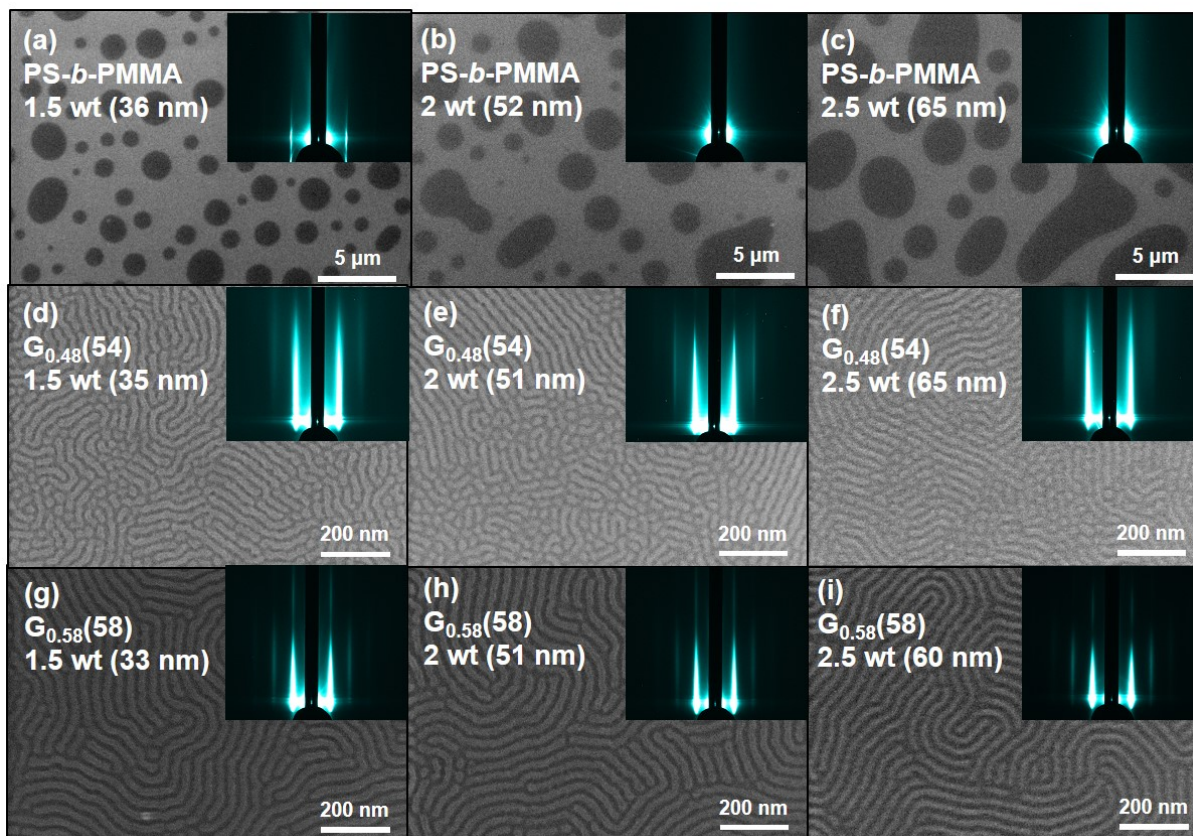


Fig. S6. Self-assembly of the block copolymers above PS-brush-treated substrate with PS-*b*-PMMA ((a)-(c)), $G_{0.48}(54)$ ((d)-(f)), and $G_{0.58}(58)$ ((g)-(i)) with different thickness (1.5~2.5 wt% in PGMEA solution). Each BCP was annealed at 300 °C, 10 min.

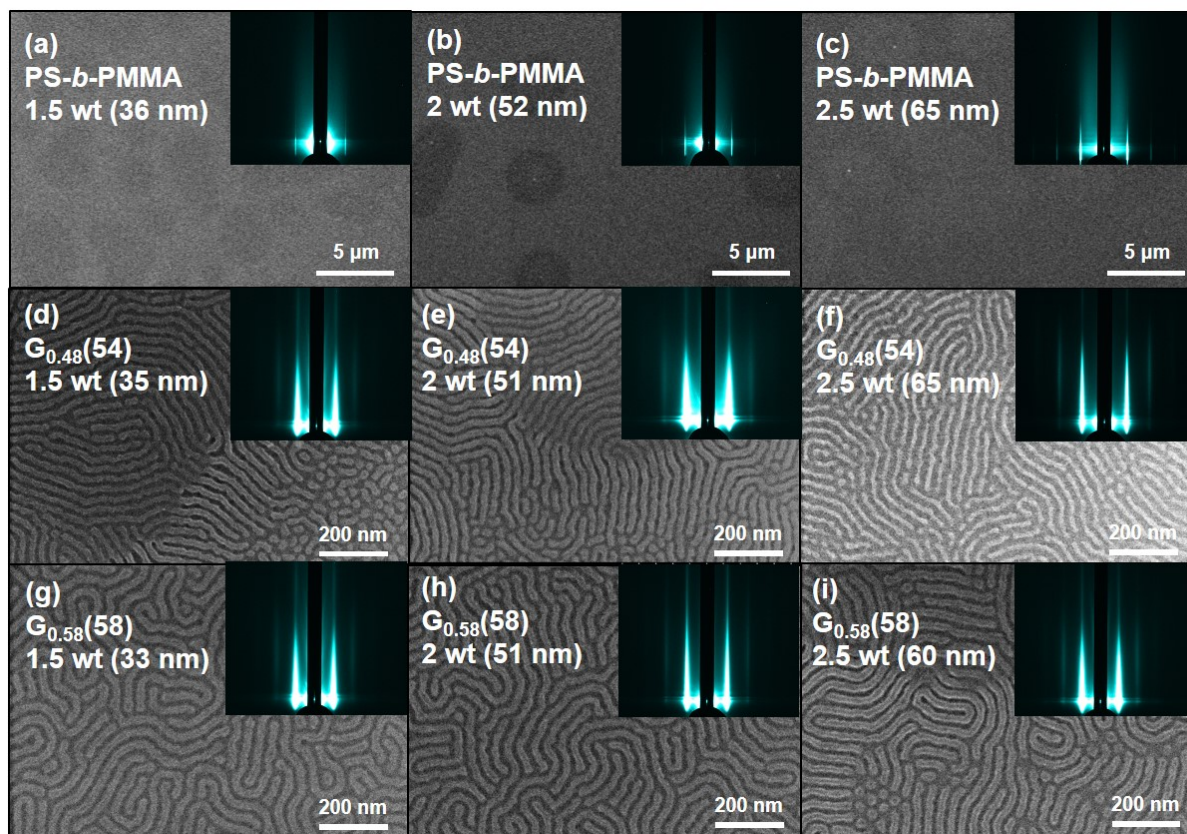


Fig. S7. Self-assembly of the block copolymers above PMMA-brush-treated substrate with PS-*b*-PMMA ((a)-(c)), $G_{0.48}(54)$ ((d)-(f)), and $G_{0.58}(58)$ ((g)-(i)) with different thickness (1.5~2.5 wt% in PGMEA solution). Each BCP was annealed at 300 °C, 10 min.

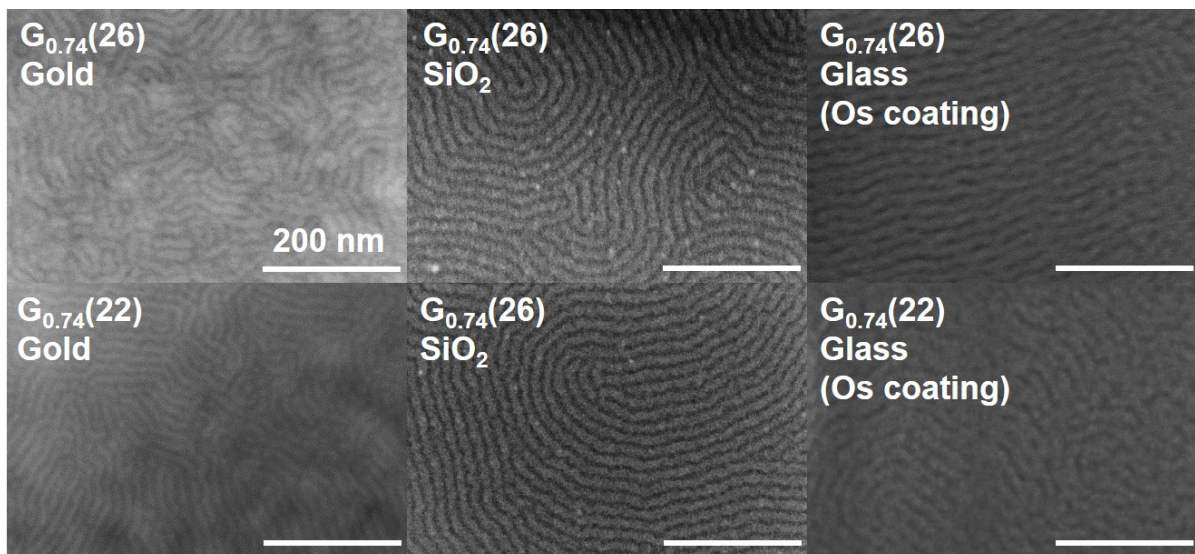


Fig. S8. Self-assembly of the block copolymers ($G_{0.74}(26)$, and $G_{0.74}(22)$) on various substrates.

Each BCP was annealed at 300 °C for 1 min.

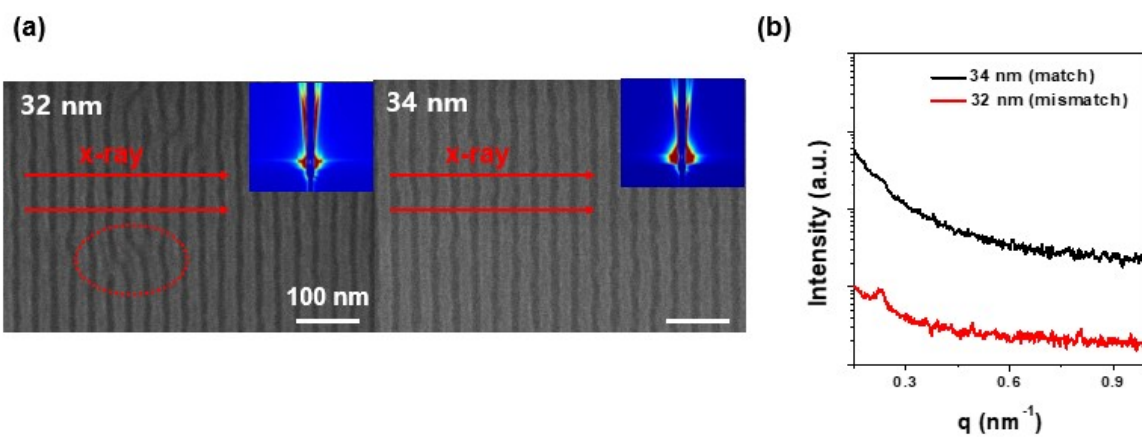


Fig. S9. GISAXS analysis result with an incidence angle of 0.12° . (The X-ray beam direction was aligned perpendicularly to the long axis of the BCP/EUV patterns.)

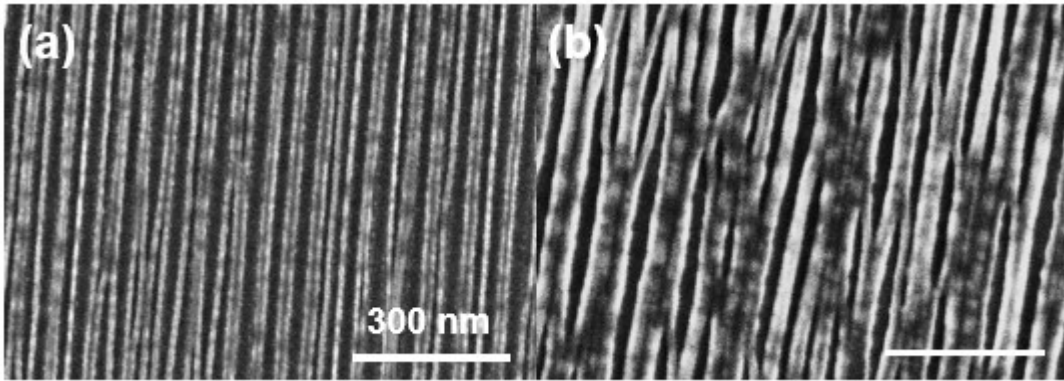


Fig. S10. SEM images of EUV PR after (a) 1 cycle and (b) 3 cycles of Bosch process. (1. SF₆, 110 W (Source) / 60 W (Bias) 30 sec, 2. C₄F₈ (100 W (Source) / 40 W (Bias) 30 sec)

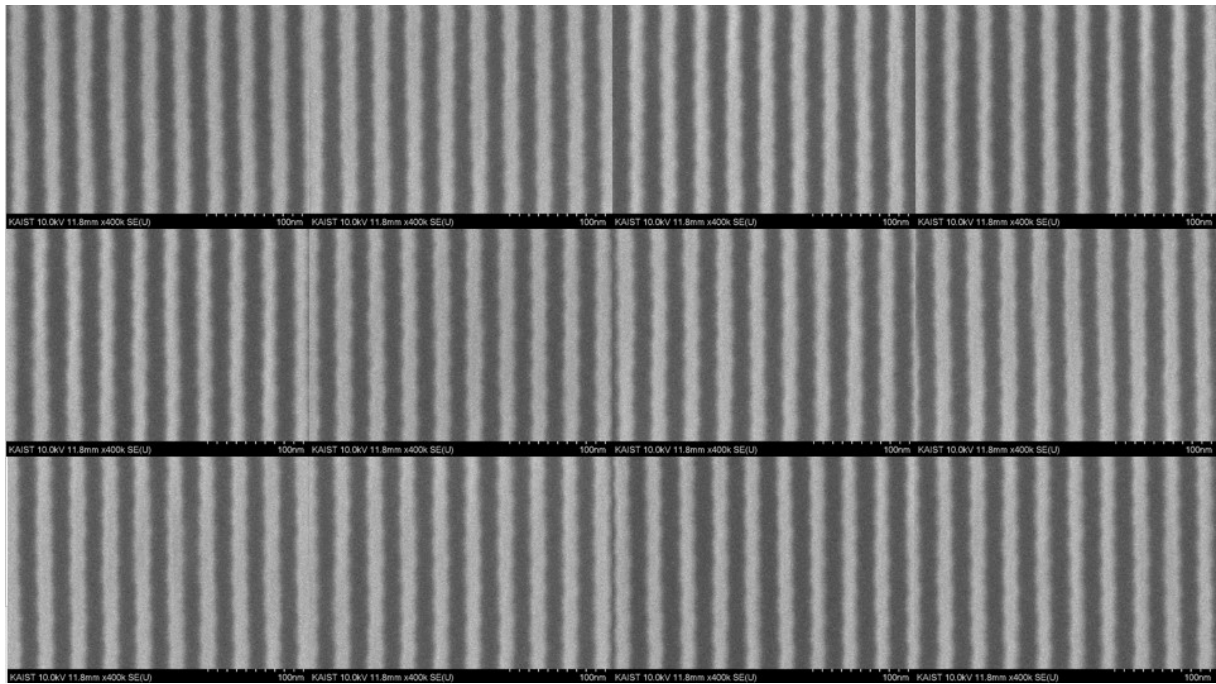


Fig. S11. SEM images used for image analysis after pattern transfer.

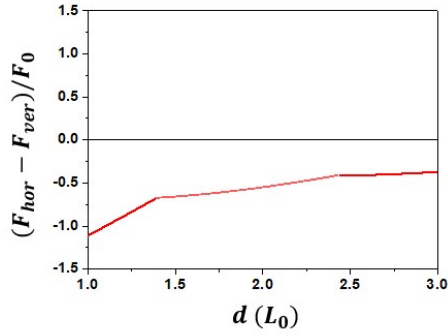
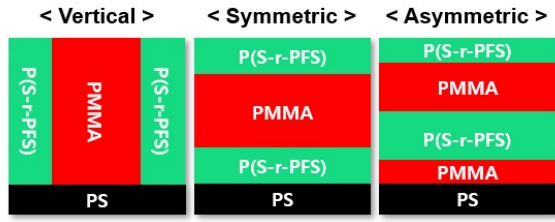
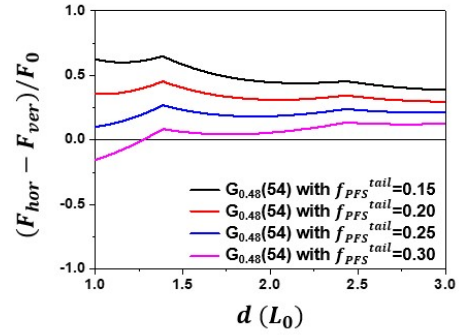
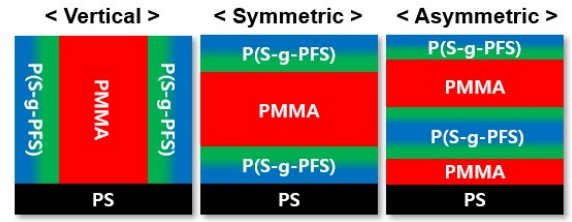
(a) Random ($f_{PFS}=0.48$)(b) $G_{0.48}(54)$ 

Fig. S12. (a) Illustrations of the BCPs with random block on PS brush. $\Delta\gamma_{Air}$ and $\Delta\gamma_{Bot}$ were calculated for three different orientations, vertical lamellae (left), symmetric horizontal lamellae (middle), and asymmetric horizontal lamellae (right). Differences of BCP thin-film free energies between the vertical and horizontal lamellar orientations $(F_{hor} - F_{ver})/F_0$ as a function of thickness d (unit of L_0) of BCPs with random block, where $f_{PFS} = 0.48$. (b) Schematics and $(F_{hor} - F_{ver})/F_0$ as a function of d of GRC-containing BCPs on PS brush with different f_{PFS}^{tail} values.

BCP	Synthesis Reaction			Result	
	[Styrene]+[PFS]	[Styrene]:[PFS]	Reaction Time	Molecular Weight	[PS]: [PPFS]
Grad _{3.73}	3.73 M	0.66: 0.34	2h	46.4 k	0.59: 0.41
Grad _{0.97}	0.97 M	0.66: 0.34	6h	52.0 k	0.60: 0.40
Grad _{0.68}	0.68 M	0.66: 0.34	24h	41.1 k	0.63: 0.47

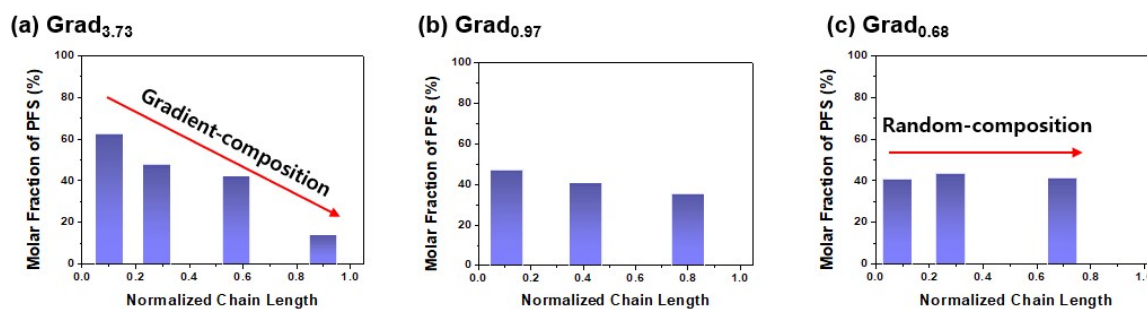


Fig. S13. Synthesis of gradient-BCP and random-BCP with variation of polymerization time. Polymers having a gradient composition were obtained with a high polymerization rate, whereas those with random composition were prepared with a relatively lower polymerization rate.

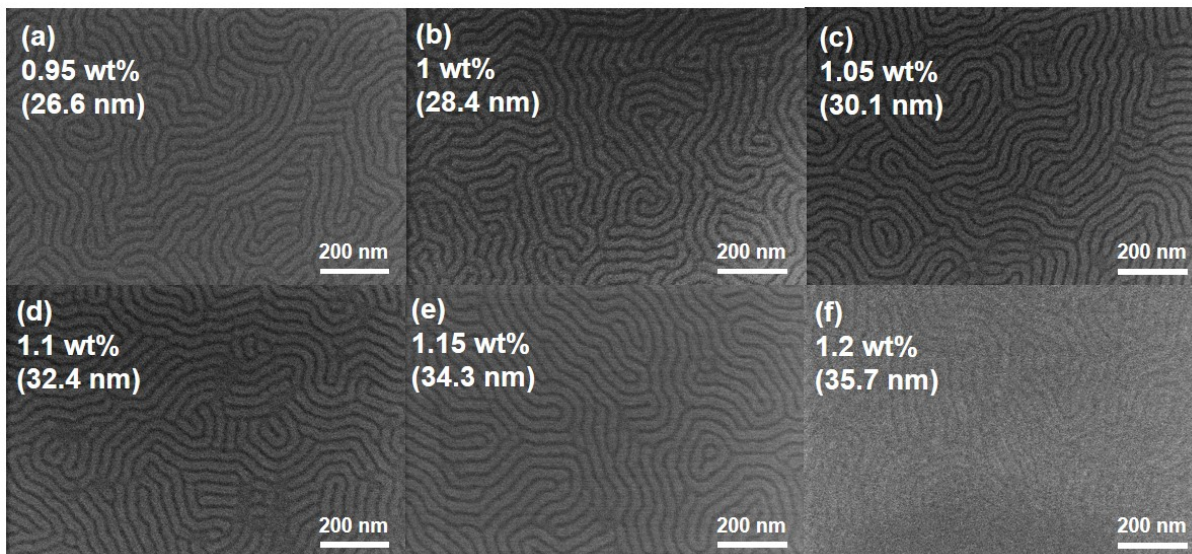


Fig. S14. Self-assembly of $R_{0.07}(45)$ (random) with different thickness (26.6 nm to 35.7 nm). Each film was annealed at 300 °C, 10 min, above P(S-*co*-MMA) neutral brush ((molar fraction of PS)=0.65).

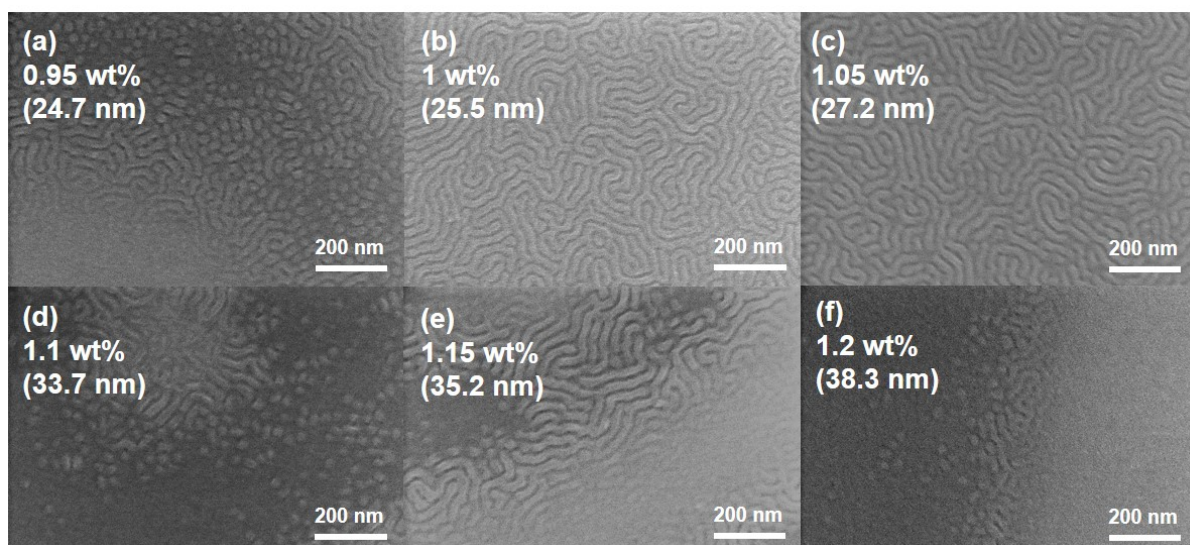


Fig. S15. Self-assembly of $R_{0.13}(43)$ (Random) with different thickness (24.7 nm to 38.3 nm). Each film was annealed at 300 °C, 6 min, above P(S-*co*-MMA) neutral brush ((molar fraction of PS)=0.81).

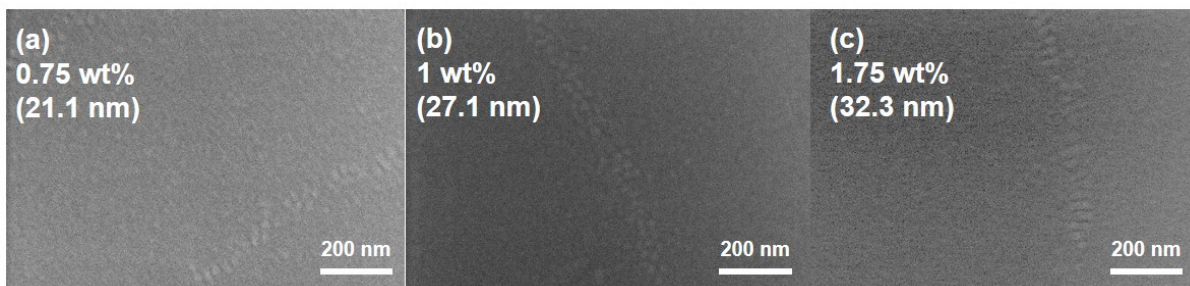


Fig. S16. Self-assembly of $R_{0.23}(44)$ (Random) with different thickness (21.1 nm to 32.3 nm).

Each film was annealed at 300 °C, 10 min, above the PS brush.

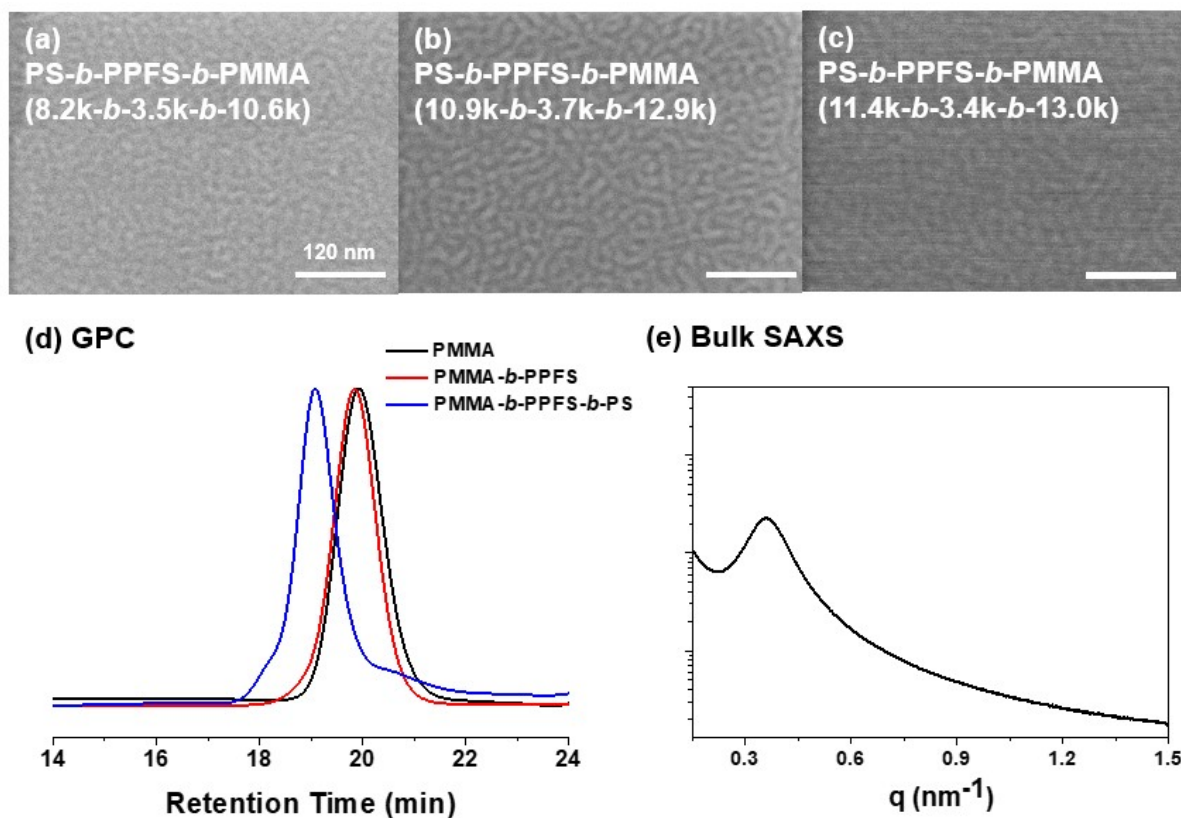


Fig. S17. Synthesis and self-assembly of PMMA-*b*-PPFS-*b*-PS. A triblock system with distinct PPFS and PS blocks but with a similar block sequence to the composition of the GRC-BCP system was synthesized and self-assembled for comparison. Triblock copolymers had undesired morphologies such as PPFS dots in the lamellar matrix, which occurs when the PPFS and PS blocks have a sufficiently high χN value to phase-separate.³ We thereby synthesized a triblock copolymer with a small volume fraction of PPFS, and in this case, the synthesized BCP did not form a sub-10 nm scale vertical lamellar structure. (See the SEM images of (a)-(c), and broad bulk SAXS peak in (e) Nevertheless, these results do not negate the possibility of triblock systems forming a sub-10 nm scale vertical lamellar structure. For example, Bang's group published triblock sub-10 nm vertical lamellar system.⁴ However, the GRC-BCP system is more efficient in realizing universal vertical alignment than triblock system. It is also crucial to point out that universal vertical lamellar alignment has not been achieved for any triblock systems.

³ Zheng W, Wang Z-G, "Morphology of abc triblock copolymers." *Macromolecules* 28(21) (1995):7215–7223

⁴ Woo, Sanghoon, et al. "Molecular tailoring of poly (styrene-*b*-methyl methacrylate) block copolymer toward perpendicularly oriented nanodomains with sub-10 nm features." *ACS Macro Letters* 6.12 (2017): 1386-1391.