Supporting Information

Morphological Evolution of Poly(solketal methacrylate)-*block*-polystyrene Copolymers in Thin Films

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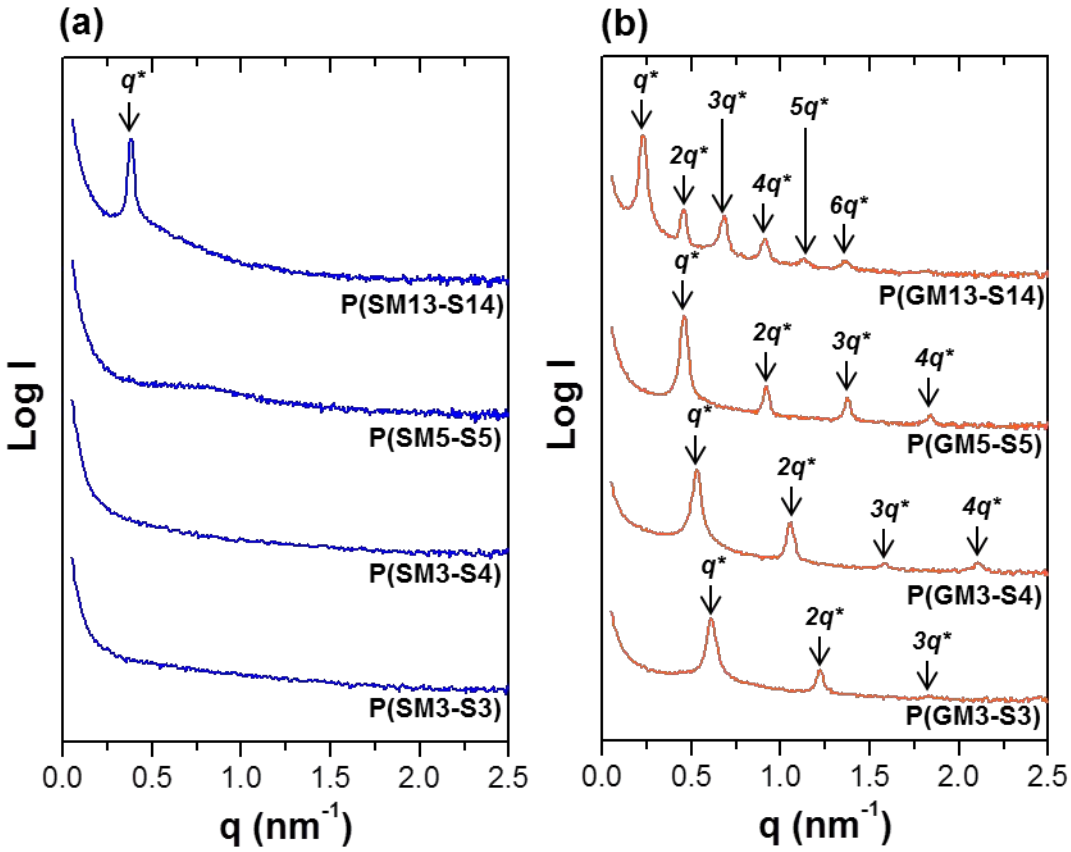

Figure S1. SAXS absolute intensity profiles for PSM-*b*-PS copolymers in bulk as a function of the scattering vector (q) (a) before and (b) after acid hydrolysis reaction.[1] The samples were thermally annealed at 140 °C for 24 h, and then measured at room temperature for 10 min. The arrows indicate the position of the primary (q*) and higher order reflections, and the intensity profiles are vertically shifted for clarity.

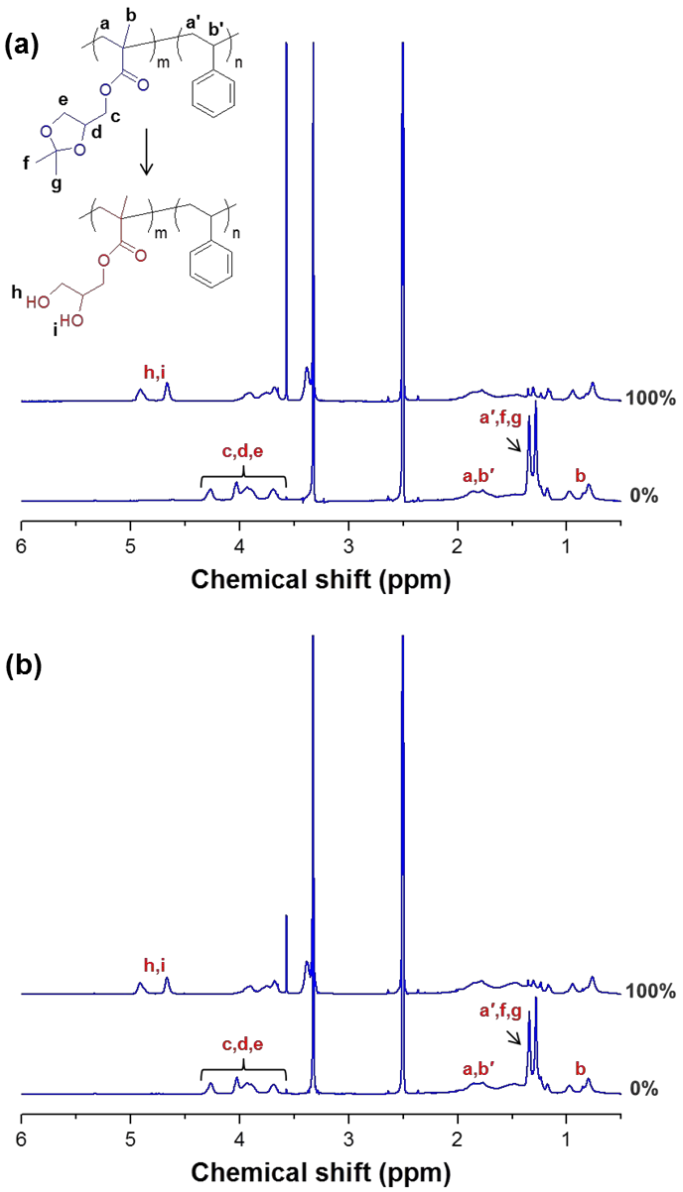

Figure S2. ^{1}H NMR spectra in DMSO-d_6 of (a) P(SM3-S4) and (b) P(SM3-S3) before and after acid hydrolysis reaction. The conversion was confirmed by the ratio of the peak areas between the methyl group of the backbone (*b*; 0.65−1.05 ppm) in SM segments and the hydroxy group (*h, i*; 4.55−4.96 ppm) in GM segments. The spectrums are vertically shifted for clarity.

Table S1. Contact angles of water and methylene iodide (MI) and surface energies of PSM, PGM, PSM-*r*-PS, and PGM-*r*-PS measured in air. The contact angles were measured at room temperature and the surface energies were calculated using Wu's method.[2,3]

Surface	Water contact angle (°)	MI contact angle (°)	γ^d (mJ/m^2)[b]	γ^p (mJ/m^2)[c]	γ (mJ/m^2)
PS[a]	-	-	33.9	6.8	40.7
PSM	72.2 ± 0.5	42.9 ± 0.3	29.4	14.3	43.7
PGM	58.1 ± 1.1	33.1 ± 0.4	31.9	20.9	52.8
PSM-*r*-PS	78.0 ± 0.4	37.3 ± 0.4	32.9	10.6	43.5
PGM-*r*-PS	66.8 ± 0.4	36.9 ± 0.6	31.4	16.1	47.5

[a]Obtained from the reference.[2] [b]Dispersion element. [c]Polar element.

Table S2. Interfacial energies of PS, PSM, and PGM with the random copolymer brush layer.

Surface	Interfacial energy with PS (mJ/m^2)	Interfacial energy with PSM or PGM (mJ/m^2)	$\Delta\gamma$ (mJ/m^2)
PSM-*r*-PS	0.8	0.7 with PSM	0.1
PGM-*r*-PS	3.9	0.6 with PGM	3.3

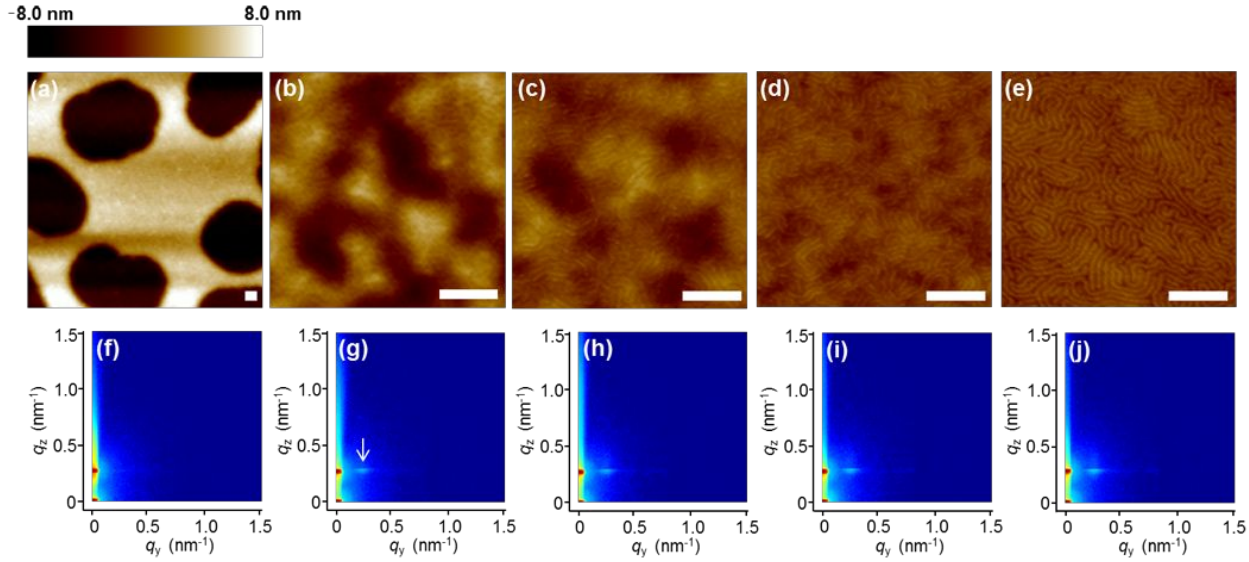

Figure S3. Morphological evolution of P(SM13-S14) (N = 197) in the thin films as a function of exposure time ranging from 0 min to 80 min to TFA vapor; (a,f) 0 min, (b,g) 20 min, (c,h) 40 min, (d,i) 60 min, and (e,j) 80 min. The samples were thermally annealed at 150 °C for 12 h, and then measured by (a−e) AFM height and (f−j) GISAXS. The color contrast is shown in the AFM height images; dark area is thinner (holes) and bright area is thicker (islands). The two dimensional (2D) GISAXS measurement was performed at room temperature for 10 min, and the incident angle (α_i) was set at 0.18°, which is larger than the critical angle of the polymer film (0.16°). The scale bars represent 250 nm.

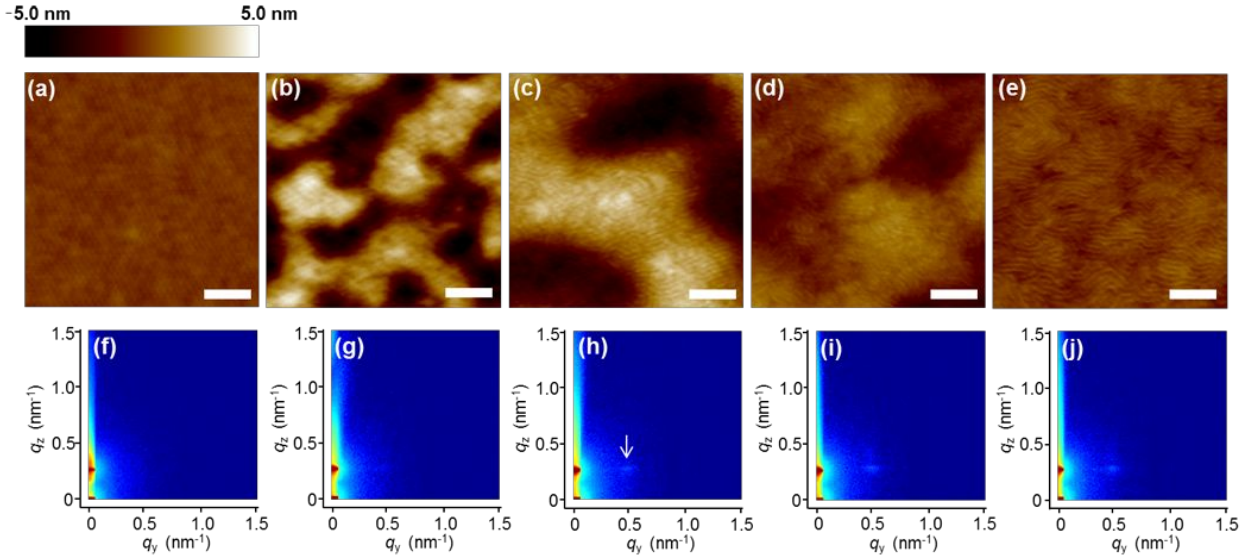

Figure S4. Morphological evolution of P(SM5-S5) (N = 76) in the thin films as a function of exposure time ranging from 0 min to 80 min to TFA vapor; (a,f) 0 min, (b,g) 20 min, (c,h) 40 min, (d,i) 60 min, and (e,j) 80 min. The samples were thermally annealed at 150 °C for 12 h, and then measured by (a−e) AFM height and (f−j) GISAXS. The color contrast is shown in the AFM height images; dark area is thinner (holes) and bright area is thicker (islands). The 2D GISAXS measurement was performed at room temperature for 10 min, and α_i was set at 0.18°. The scale bars represent 100 nm.

REFERENCES

[1] Yu, D. M.; Mapas, J. K. D.; Kim, H.; Choi, J.; Ribbe, A. E.; Rzayev, J.; Russell, T. P. Evaluation of the Interaction Parameter for Poly(solketal methacrylate)-*block*-polystyrene Copolymers. *Macromolecules* **2018**, 51, 1031-1040.

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[3] Thomas, S.; Thomas, S.; Abraham, R.; Bandyopadhyay, S. Polystyrene/Calcium Phosphate Nanocomposites: Contact Angle Studies Based on Water and Methylene Iodide. *Express Polym Lett* **2008**, 2, 528-538.