Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Chemically tailored high-χ block copolymers for perpendicular lamellae via thermal annealing

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Synthesis of PGMA by living anionic polymerization

All polymerization procedures were performed under an argon atmosphere. Here, 50 mL of THF and LiCl (23.1 mg, 0.545 mmol) were transferred to a 100-mL Schlenk flask and cooled to −78 °C. *Sec*-butyllithium was added until the solution turned light yellow. The Schlenk flask was removed from the cooling bath and allowed to reach room temperature, causing the solution to become colorless. The Schlenk flask was cooled backed to −78 °C, and *sec*-BuLi solution in cyclohexane and *n*-hexane (0.108 mL, 0.109 mmol) was added. DPE (0.0954 mL, 0.545 mmol) was added, resulting in a deep red color. After 30 min of stirring, GMA (2.00 mL, 15.2 mmol) was added and stirred for 5 min. The solution became colorless. Then, the Schlenk flask was transferred to −40 °C cooled bath and stirred 30 min. Then 5 mL of MeOH (excess amount) was added to the Schlenk flask to prepare the proton-terminated PGMA. The polymer was precipitated into MeOH and filtered, and then the product was dried under a reduced pressure at 40 °C overnight to yield PGMA as a white powder (1.88 g, 91 % yield). The M_n and $Đ$ of the product tested by SEC were 14 200 g mol^{-1} and 1.12, respectively. ^{1}H NMR (400 MHz, acetone-d_6, δ, ppm): 0.98 (s, α-CH_3), 1.14 (s, α-CH_3), 1.98 (br, backbone, -CH_2-C(CH$_3$)-), 2.70 (s, -CH$_2$-CH(CH_2)-O-), 2.84 (s, -CH$_2$-CH(CH_2)-O-), 3.28 (s, -CH$_2$-CH(CH$_2$)-O-), 3.84 (s, -(C=O)O-CH_2-), 4.37 (s, -(C=O)O-CH_2-). ^{13}C NMR (100 MHz, acetone-d_6, δ, ppm): 17.3, 19.5, 44.8, 45.6, 46.0, 49.6, 52.8, 54.9, 66.8, 176.5, 177.8.

Synthesis of PHEtMA and PHFMA through the post-functionalization of PGMA

The general procedure of the post-functionalization of PGMA is as follows. A 10-mL round bottom flask was charged with PGMA and DMF (10 mole equiv. to PGMA repeating units) and immersed in an ice-water bath. TEA (2 mole equiv.) and thiol (2 mole equiv.) were added to the flask. After 30 min, the flask was transferred to an oil bath set to 40 °C and stirred 24 h. The crude solution was diluted with THF, precipitated from an MeOH/water mixture, and then filtered to collect the precipitate. After filtration, the solid was dissolved in THF, precipitated from an MeOH/water mixture, and then filtered 2 or 3 times to remove the residual reagents. The product was dried under a reduced pressure at room temperature overnight to yield a white powder (30–50 % yield).

Characterization of PHEtMA. The M_n and $Đ$ of the product measured by SEC were 21 000 g mol^{-1} and 1.13, respectively. ^{1}H NMR (400 MHz, acetone-d_6, δ, ppm): 0.98 (s, α-CH_3), 1.13 (s, α-CH_3), 1.29 (t, -S-CH$_2$-CH_3), 1.95 (br, backbone, -CH_2-C(CH$_3$)-), 2.55–2.71 (q, -S-CH_2-CH$_3$), 2.72–2.90 (m, -CH_2-S-), 3.90–4.22 (m, -(C=O)O-CH_2-CH(OH)-), 4.35 (s, -OH). ^{13}C NMR (100 MHz, acetone-d_6, δ, ppm): 15.4, 17.8, 19.6, 27.1, 36.3, 45.7, 52.6, 54.7, 68.5, 69.4, 177.4, 178.0.

Characterization of PHFMA. The M_n and $Đ$ of the product measured by SEC were 27 700 g mol^{-1} and 1.19, respectively. ^{1}H NMR (400 MHz, acetone-d_6, δ, ppm): 0.97 (s, α-CH_3), 1.11 (s, α-CH_3), 1.81–2.13 (br, backbone, -CH_2-C(CH$_3$)-), 2.86–3.05 (m, -CH_2-S-), 3.40–3.61 (q, -S-CH_2-CF$_3$), 3.92–4.26 (m, -(C=O)O-CH_2-CH(OH)-), 4.59 (s, -OH). ^{13}C NMR (100 MHz, acetone-d_6, δ, ppm): 17.9, 19.6, 34.4, 34.7, 35.0, 35.4, 37.0, 45.7, 46.0, 52.3, 54.2, 68.3, 69.7, 123.4, 126.2, 128.9, 131.6, 178.0.

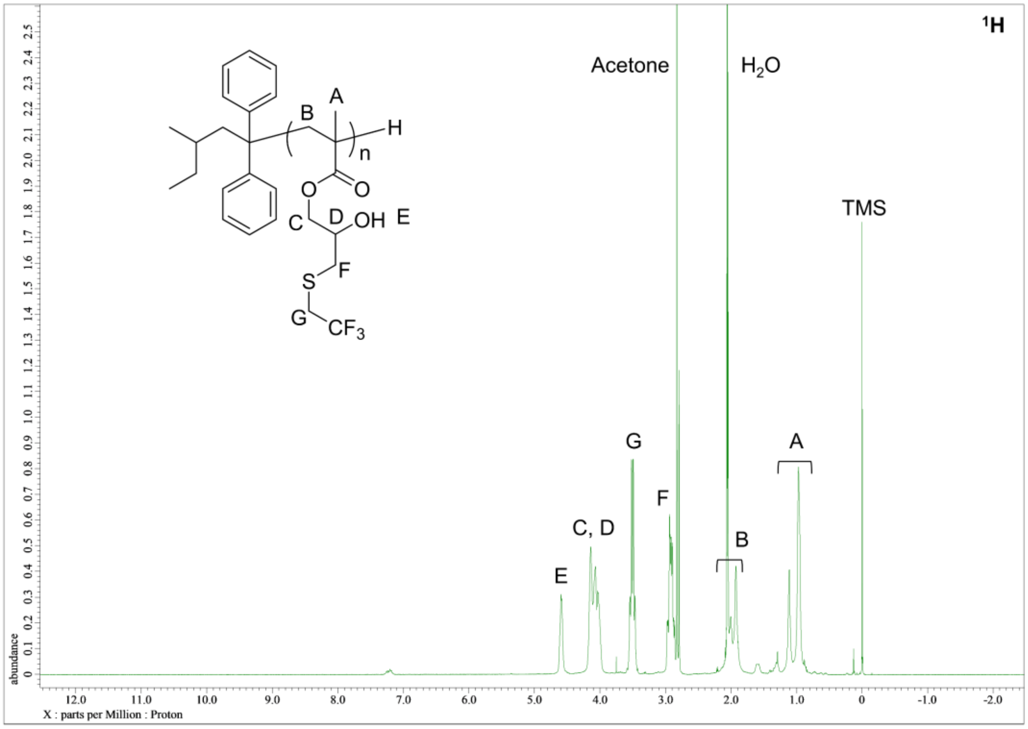

Fig. S1 (A) ^{1}H NMR spectrum of PHFMA.

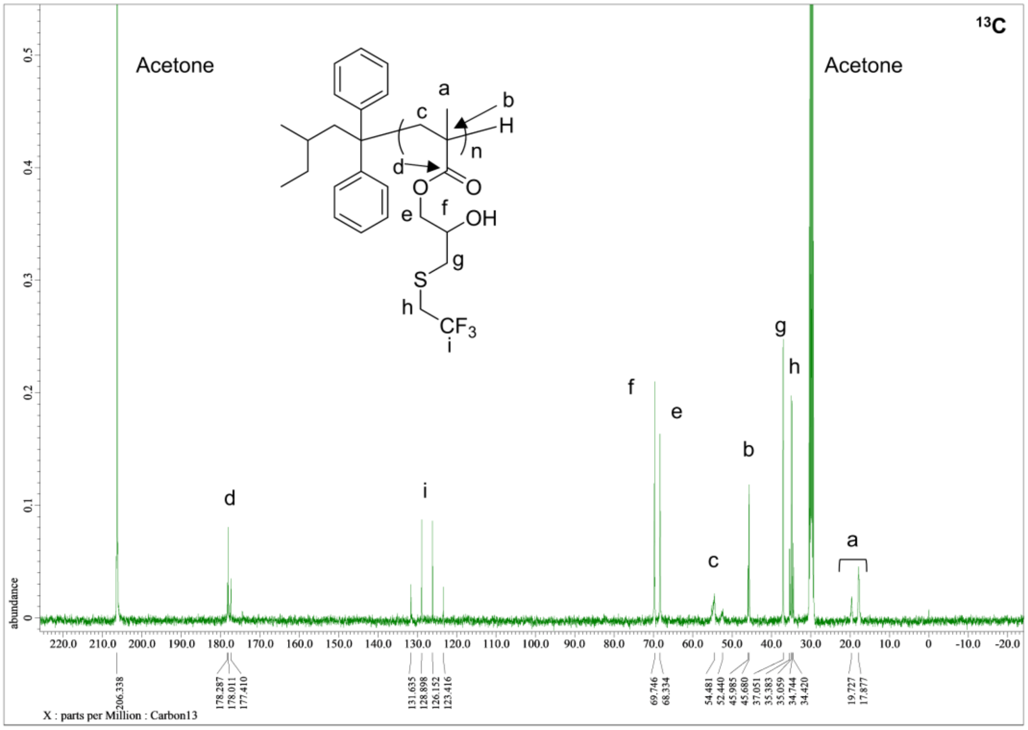

Fig. S1 (B) ^{13}C NMR spectrum of PHFMA.

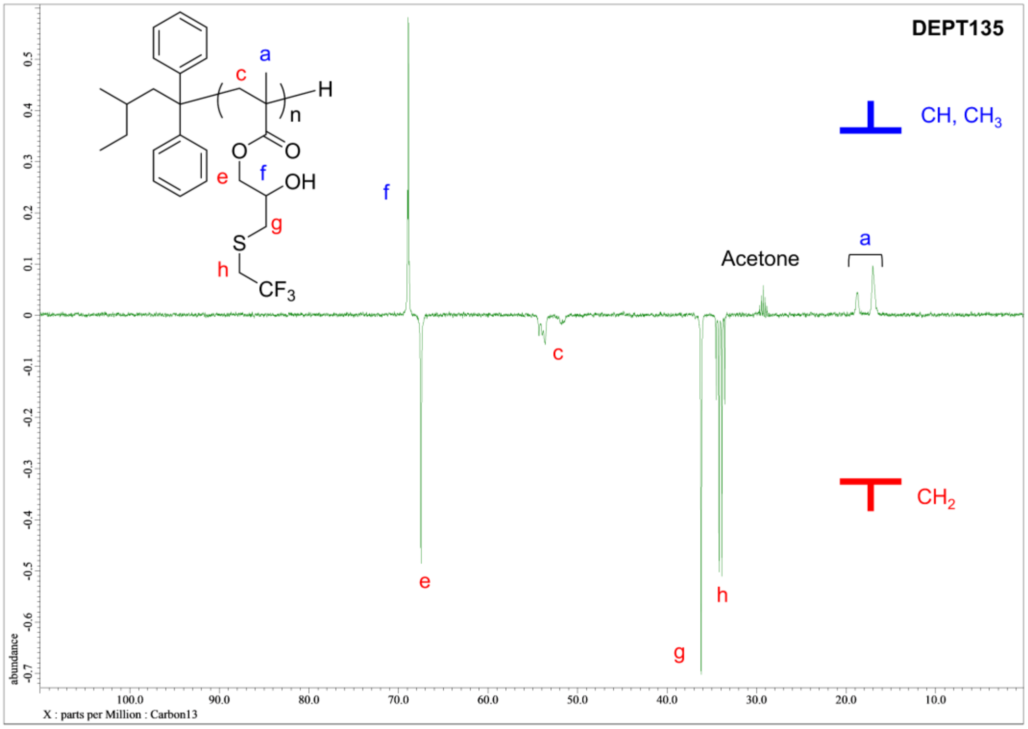

Fig. S1 (C) DEPT135 NMR spectrum of PHFMA.

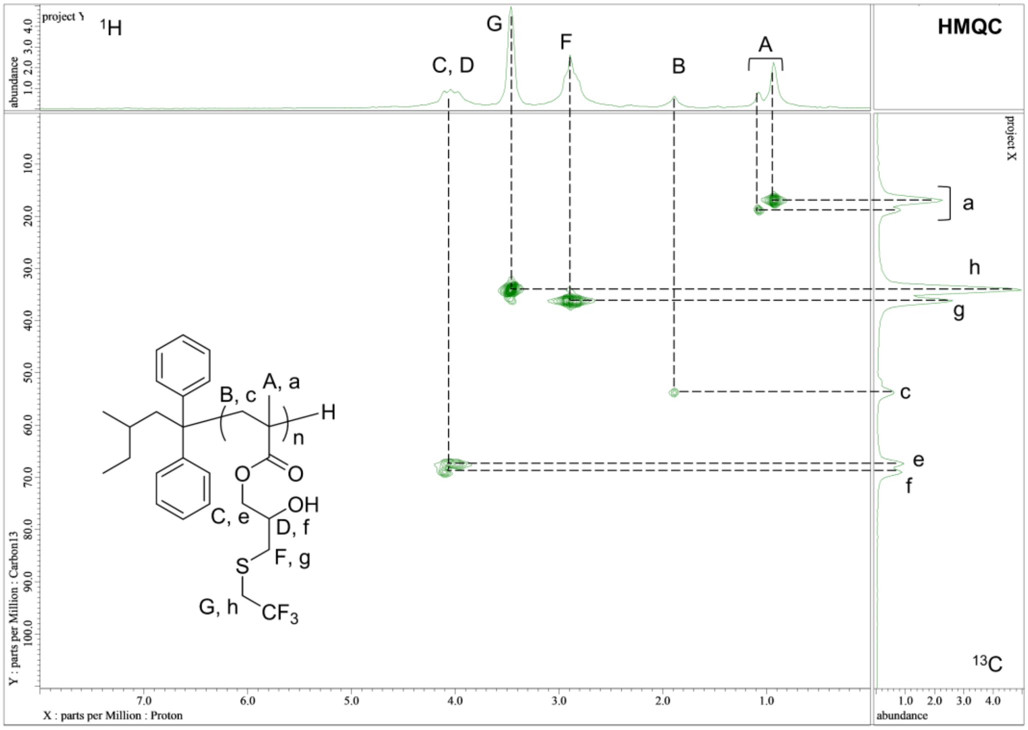

Fig. S1 (D) HMQC NMR spectrum of PHFMA.

Synthesis of PS-*r*-PMMA-*r*-PGMA by free radical polymerization

2,2’-Azobis(isobutyronitrile) (0.1 g, 0.61 mmol), styrene (1.14 mL, 10 mmol), methyl methacrylate (1.04 mL, 9.8 mmol) and GMA (0.026 mL, 0.20 mmol) were added to a 20-mL Schlenk tube, and the solution was degassed by three freeze-pump-thaw cycles and backfilled with nitrogen. The solution was stirred at 80 °C for 2 h. The polymerization was quenched by rapid cooling with liquid nitrogen. The crude product was diluted with CH_2Cl_2, precipitated from MeOH, and then filtered to collect the precipitate. After filtration, the product was dried under a reduced pressure at 40 °C overnight to yield PS-*r*-PMMA-*r*-PGMA as a white powder (1.85 g, 91 % yield). The M_n and $Đ$ of the product tested by SEC are 17 400 g mol^{-1} and 2.05, respectively. ^{1}H NMR (400 MHz, chloroform-*d*, *δ*, ppm): 0.24–1.02, 1.08–1.34, 1.37–2.08, 2.09–2.49, 2.62–3.04, 3.10–3.68, 6.40–7.31. ^{13}C NMR (100 MHz, chloroform-*d*, *δ*, ppm): 18.1, 19.9, 21.4, 38.7, 44.1, 45.3, 50.6, 125.9, 128.1, 144.7, 176.2.

DSC analysis of the homopolymers

The glass transition temperatures (T_g) of homopolymers were determined via DSC in the second heating cycle. Baseline-shifts were observed in DSC curves of PGMA, PHEtMA, and PHFMA at 68 °C, 25 °C, and 37 °C, respectively.

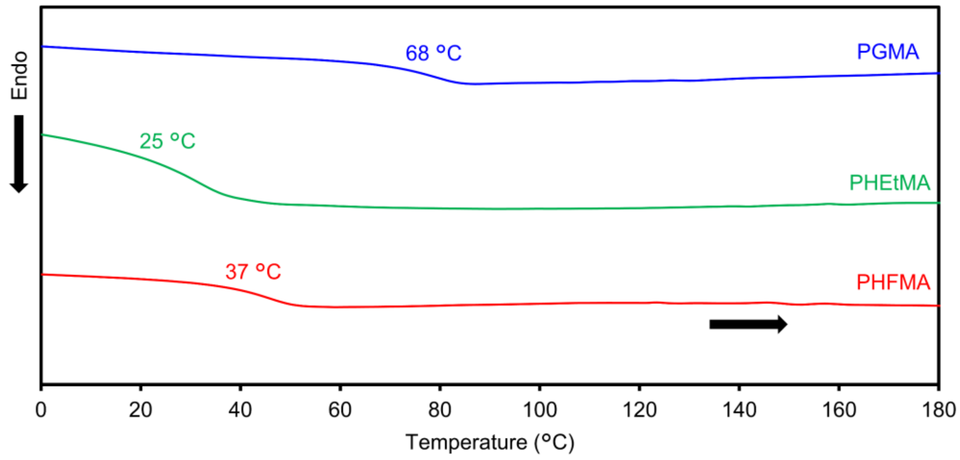

Fig. S2 DSC curves of PGMA, PHEtMA, and PHFMA in the second heating cycle.

Determining the homopolymer densities by gradient column

The densities of PHEtMA and PHFMA were determined by placing each homopolymer into a gradient column prepared from aqueous KI solution calibrated with organic reagents of known densities. The reagents used, positions on the graduated cylinder, and estimated densities were summarized in Table S1 (A: PHEtMA and B: PHFMA).

Table S1 (A) The positions on the graduate cylinder and densities of the organic reagents for the calibration of gradient column to determine the density of PHEtMA.

Reagents	Position on graduate cylinder (mL)	Density (g cm^{-3})
PHEtMA	150	1.23
Phenylether	85	1.07
Chlorobenzene	97	1.11
Nitrobenzene	138	1.20
1,2-Dichloroethane	164	1.26
Dichloromethane	215	1.33

Table S1 (B) The positions on the graduate cylinder and densities of the organic reagents for the calibration of gradient column to determine the density of PHFMA.

Reagents	Position on graduate cylinder (mL)	Density (g cm^{-3})
PHFMA	125	1.43
1-Bromohexane	65	1.18
Nitrobenzene	70	1.20
1,2-Dichloroethane	81	1.26
2-Bromoethylbenzene	108	1.38
1,9-Dibromononane	119	1.41
Chloroform	132	1.49
1,7-Dibromoheptane	159	1.53
1-Bromo-4-fluorobenzene	216	1.59

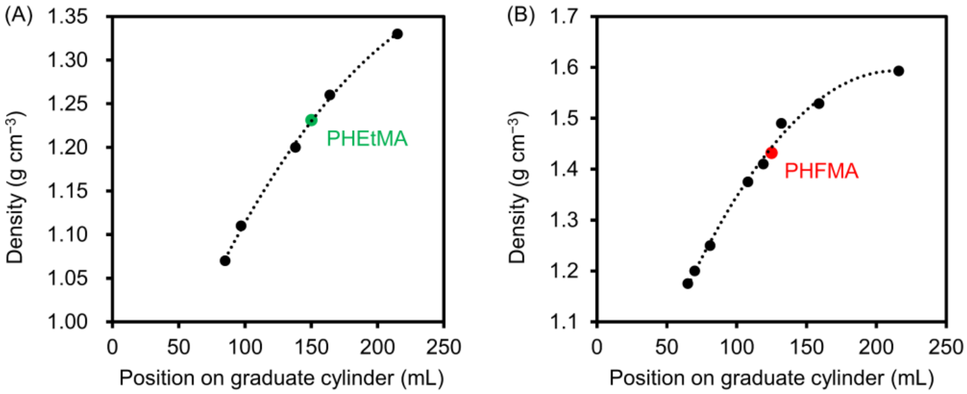

Fig. S3 Estimating the densities of the synthesized homopolymers (A: PHEtMA and B: PHFMA) by gradient column.

Estimating the surface free energies of the homopolymers

The surface free energies (SFEs) of the homopolymers were calculated by measuring the water and diiodomethane contact angles (C.A.) of the homopolymer thin films. The thin films were prepared by spin-coating a 10 wt.% propyleneglycol monomethyl ether acetate (PGMEA) solution on bare silicon wafers at 3000 rpm for 30 s to obtain thin films with thicknesses of 200–400 nm. These thin films were annealed at 120 °C for 10 min before the C.A. measurements.

Table S2 Contact angles and surface free energies (SFEs) of homopolymers.

Homopolymer	C.A. (H_2O)[a] (°)	C.A. (CH_2I_2)[a] (°)	SFE[b] ($mJ\ m^{-2}$)
PGMA	62.9 ± 0.9	24.9 ± 0.7	51.1
PHEtMA	73.7 ± 0.4	34.9 ± 0.8	44.2
PHFMA	80.5 ± 0.7	56.8 ± 2.2	33.3
PS[c]	90.5 ± 0.8	–[d]	–[d]

[a] Average values of measurements taken at 5 positions. [b] Calculated by the Owens–Wendt method. [c] The C.A. measurement for PS used a homopolymer with M_n = 34.6 kg mol^{-1} and $Đ$ = 1.09, prepared through anionic polymerization. [d] The SFE of PS could not be obtained as PS was partially soluble in diiodomethane.

FT-IR analysis of the synthesized BCPs

The FT-IR spectra for each BCP were taken using potassium bromide (KBr) as the matrix.

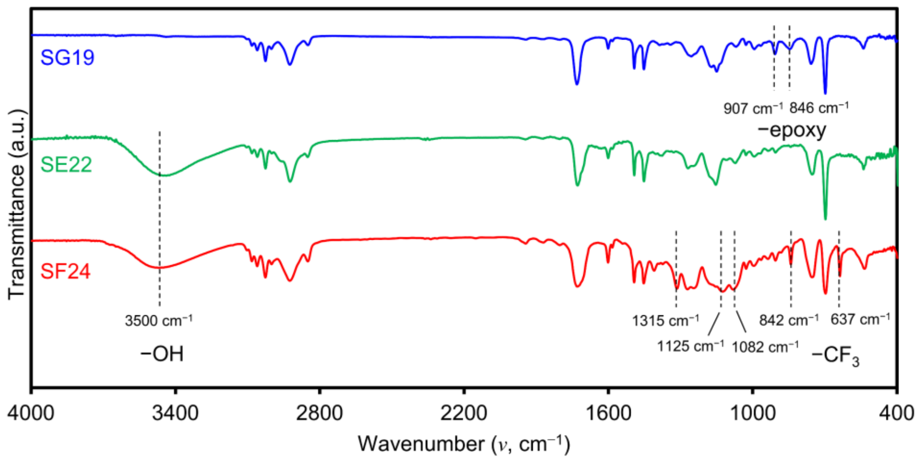

Fig. S4 FT-IR spectra of SG19, SE22, and SF24.

Temperature-dependent SAXS analyses of SG10, SE11, and SF6

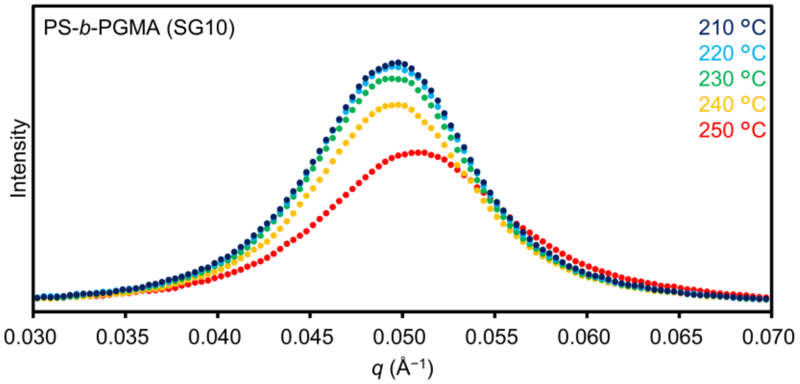

Fig. S5 (A) The scattering profiles measured by SAXS at different temperatures for PS-*b*-PGMA (SG10).

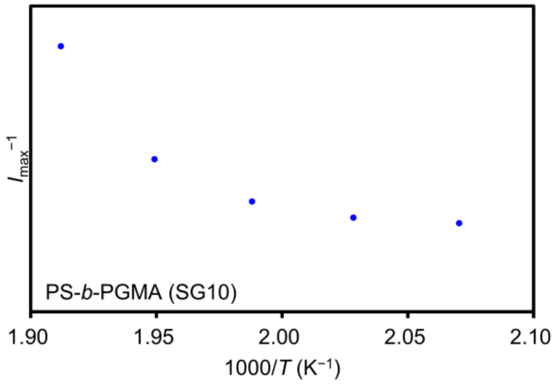

Fig. S5 (B) The I_{max}^{-1}–T^{-1} plots for PS-*b*-PGMA (SG10).

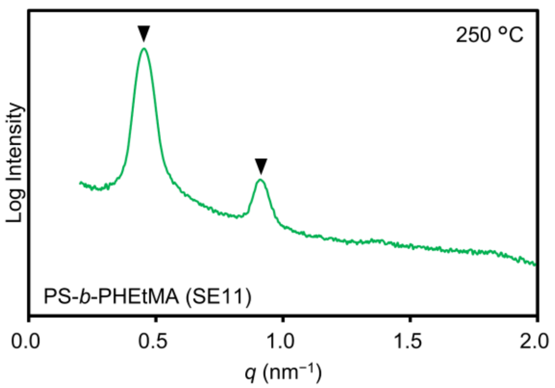

Fig. S5 (C) The SAXS profile of PS-*b*-PHEtMA (SE11) measured at 250 °C.

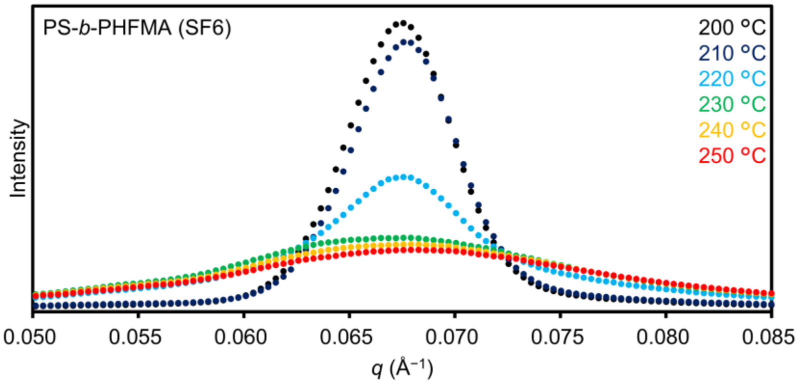

Fig. S5 (D) The scattering profiles measured by SAXS at different temperatures for PS-*b*-PHFMA (SF6).

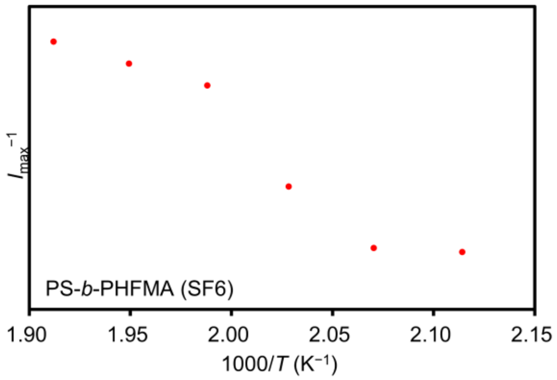

Fig. S5 (E) The $I_{\max}{}^{-1}$–T^{-1} plots for PS-*b*-PGMA (SF6).

Detailed information about the estimation of χ_{eff}

Molten BCP samples were placed in 0.01 mm thick glass tubes and the SAXS profiles were collected at each temperature in 10 °C decrement in cooling cycles, at which the temperature was maintained for 30 min prior to the measurements to reach a thermally equilibrated state. The scattering function $I(q)$ from the disordered melt of the BCPs with a dispersity in the molecular weight and asymmetry in the segmental volume was summarized below, where A_0 is a fitting constant, $S(q)$ and $W(q)$ together are correlation functions of the BCP, $g(q)$ is a modified Debye function and $y(q)$ is a dimensionless wave vector, r_c is the molar volume normalized over the degree of polymerization of the BCP, f_X is volume fraction of X calculated using the bulk densities for each block (1.05 g cm^{-3} for PS, 0.805 g cm^{-3} for PGMA, 1.23 g cm^{-3} for PHEtMA, and 1.43 g cm^{-3} for PHFMA), v_X is the molar volume of X. N_X is the degree of polymerization normalized over a common reference volume (v_0 = 118 Å^3) for X, FW is the formula weight of X, N_A is Avogadro's constant, and b_X is the segmental length of X. Here we assumed the dispersities for each homopolymer segment ($Đ_X$) are equal and were estimated from the M_w/M_n of the BCP and weight fraction of X (w_X). Four parameters, including b_X for both polymers, A_0 and χ_{eff}, were optimized in a least-squares fit to the SAXS profiles at a certain temperature. The calculated parameters for each sample were summarized in Table S3 and S4. Discontinuous changes attributed to the transition from mean-field to non-mean-field type disordered states were observed at 190–200 °C for SG4 and SF4, and 200–210 °C for SE5 in the $I_{\max}{}^{-1}$–T^{-1} plots for each sample (Fig. S6). Therefore, the estimation of χ_{eff} for each sample was done at temperatures higher than the transition.

$$I(q) = \frac{A_0}{\frac{S(q)}{W(q)} - 2\chi}$$

$$S(q) = \langle S_{PS,PS}\rangle + 2\langle S_{PS,Y}\rangle + \langle S_{Y,Y}\rangle$$

$$W(q) = \langle S_{PS,PS}\rangle \cdot \langle S_{Y,Y}\rangle - \langle S_{PS,Y}\rangle^2$$

$$\langle S_{X,X}(q)\rangle = r_c {f_X}^2 {g^{(2)}}_X(q) \quad \langle S_{PS,Y}(q)\rangle = r_c f_{PS} f_Y {g^{(1)}}_{PS}(q) {g^{(1)}}_Y(q)$$

$$r_c = \frac{(v_{PS}N_{PS} + v_Y N_Y)}{(v_{PS} \cdot v_Y)^{1/2}} \quad v_X = \frac{FW_X}{\rho_X N_A} \quad N_X = \frac{v_X M_{\mathrm{n},X}}{v_0 FW_X}$$

$${g^{(1)}}_X(q) = \frac{1}{y_X(q)} \cdot \left\{1 - [y_X(q) \cdot (\mathrm{Đ}_X - 1) + 1]^{-(\mathrm{Đ}_X - 1)^{-1}}\right\}$$

$${g^{(2)}}_X(q) = \frac{2}{y_X(q)^2} \cdot \left\{-1 + y_X(q) + [y_X(q) \cdot (\mathrm{Đ}_X - 1) + 1]^{-(\mathrm{Đ}_X - 1)^{-1}}\right\}$$

$$y_X(q) = \frac{N_X {b_X}^2}{6} q^2 \quad \mathrm{Đ} \equiv \mathrm{Đ}_{PS} = \mathrm{Đ}_Y = \frac{M_{\mathrm{w}}/M_{\mathrm{n}} - 1}{{w_{PS}}^2 + {w_Y}^2} + 1$$

X= PS or Y (Y= PGMA, PHEtMA or PHFMA).

Table S3 The fixed parameters used to estimate χ_{eff} for each sample.

BCPs	r_c	M_{n} (g mol^{-1})	M_{w} (g mol^{-1})	$M_{\mathrm{n,\,PS}}{}^{a}$ (g mol^{-1})	f_{PS}	w_{PS}
PS-*b*-PGMA (SG4)	60	4400	5500	3200	0.65	0.71
PS-*b*-PHEtMA (SE5)	65	5400	6800	3400	0.66	0.62
PS-*b*-PHFMA (SF4)	43	3700	4400	1800	0.52	0.44

[a] The molecular weight of *sec*-butyl from the initiator and DPE were counted as PS chain.

Table S4 The estimated χ_{eff} values for each sample at different temperatures.

T (°C)	Estimated χ_{eff}		
	PS-*b*-PGMA (SG4)	PS-*b*-PHEtMA (SE5)	PS-*b*-PHFMA (SF4)
200	0.1315	–	0.1673
210	0.1307	0.1268	0.1666
220	0.1303	0.1261	0.1658
230	0.1295	0.1253	0.1649
240	0.1290	0.1249	0.1641
250	0.1282	0.1241	0.1635

Table S5 Estimated enthalpic and entropic contributions for PS-*b*-PGMA (SG4), PS-*b*-PHEtMA (SE5), and PS-*b*-PHFMA (SF4).

BCP	Label	A/T	B
PS-*b*-PGMA	SG4	$16.0/T$	0.0978
PS-*b*-PHEtMA	SE5	$16.9/T$	0.0918
PS-*b*-PHFMA	SF4	$19.4/T$	0.126

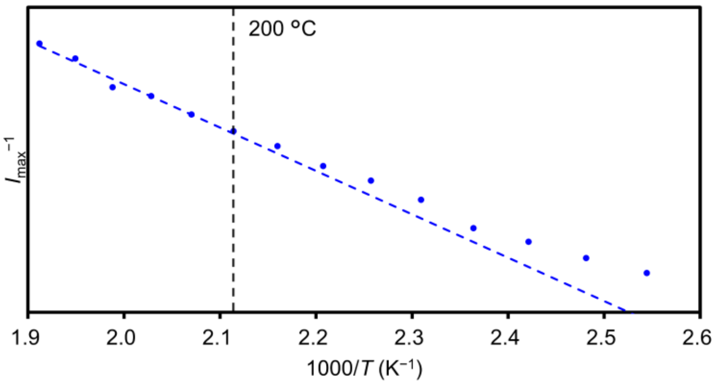

Fig. S6 (A) The I_{max}^{-1}–T^{-1} plots for PS-*b*-PGMA (SG4).

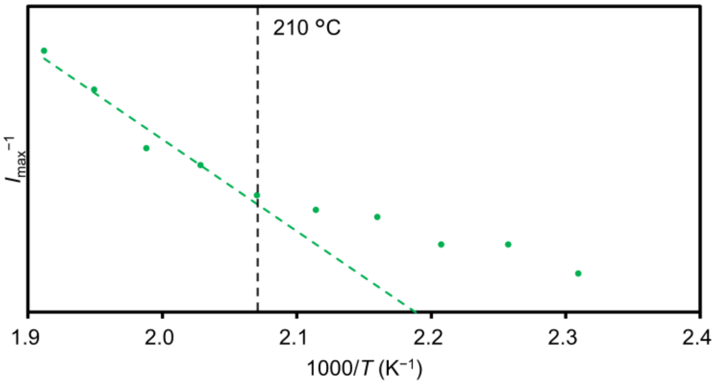

Fig. S6 (B) The I_{max}^{-1}–T^{-1} plots for PS-*b*-PHEtMA (SE5).

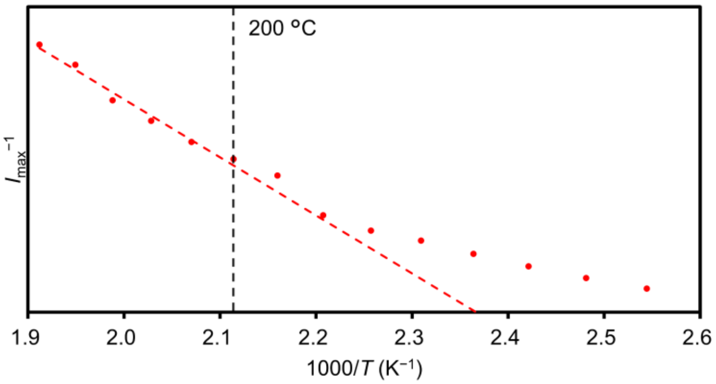

Fig. S6 (C) The I_{max}^{-1}–T^{-1} plots for PS-*b*-PHFMA (SF4).

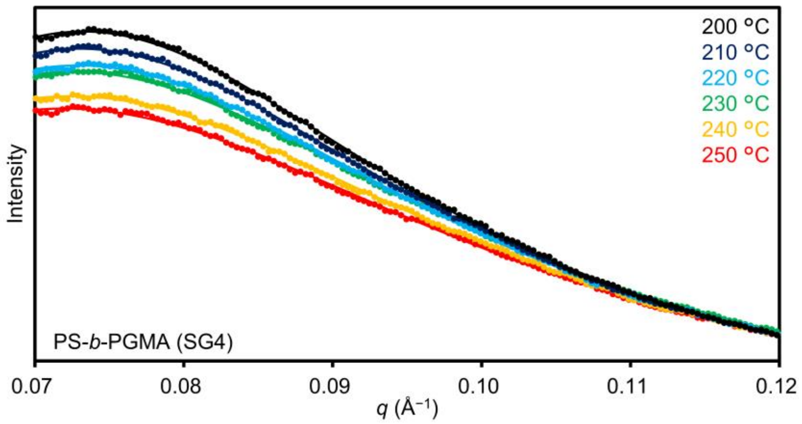

Fig. S7 (A) The scattering profiles (dots) measured by SAXS and the fitting profiles (lines) at different temperatures for PS-*b*-PGMA (SG4).

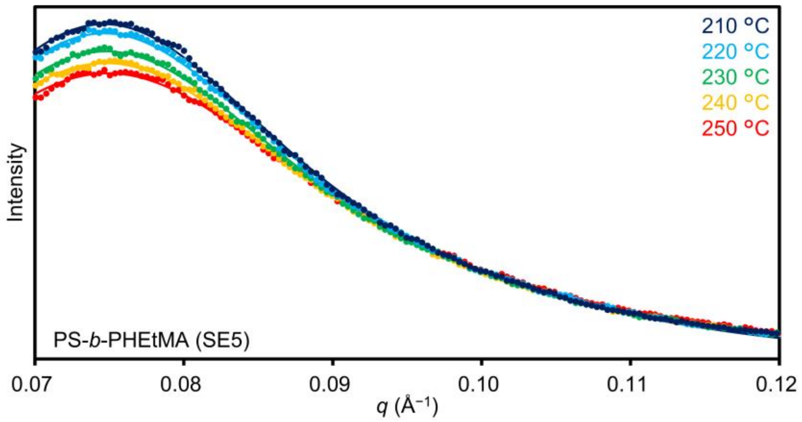

Fig. S7 (B) The scattering profiles (dots) measured by SAXS and the fitting profiles (lines) at different temperatures for PS-*b*-PHEtMA (SE5).

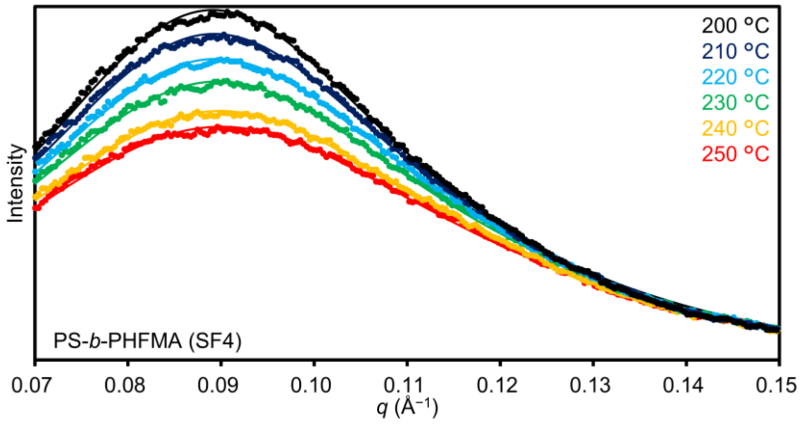

Fig. S7 (C) The scattering profiles (dots) measured by SAXS and the fitting profiles (lines) at different temperatures for PS-*b*-PHFMA (SF4).

Etch contrast in O_2-RIE

The etch resistances against O_2-RIE treatment for PS and PHFMA were obtained using thin films of the homopolymers. The thin films were prepared by spin-coating PGMEA solutions onto bare silicon wafers to produce approximately 250-nm films. The PHFMA film was removed at twice the rate of PS.

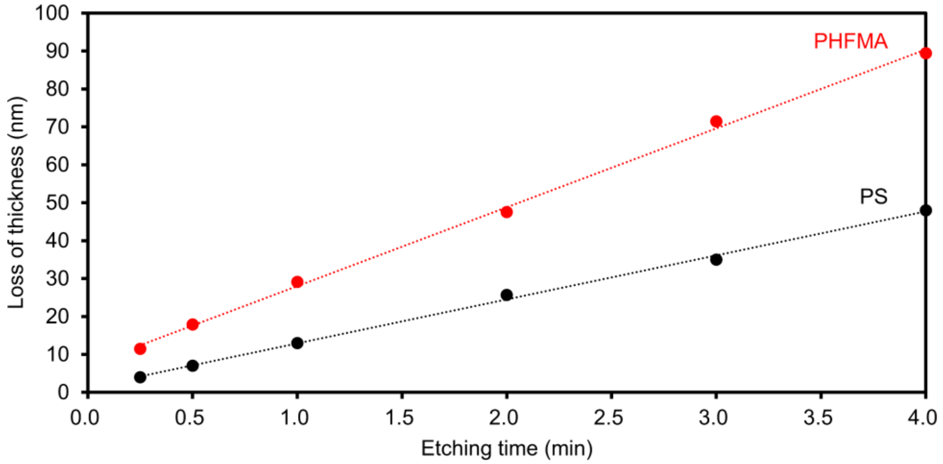

Fig. S8 Graph of film thickness removed as a function of time for the PS and PHFMA thin films during O_2-RIE treatment.