Supporting Information

Control of Microphase-Separated Structures by Tuning the Functional Groups and the Degree of Modification for a Single BCP

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Synthesis

PAGE: ¹H NMR (400 MHz, CDCl₃, δ, ppm) = 2.30-2.33 (S, *CH*₃-C₆H₆-), 3.46-3.52 (m, -*CH*₂-O-, 2H), 3.40-3.49 (m, -O-*CH*₂-CH(OH)-*CH*₂-O, PAGE), 3.96-3.98 (d, -CH₂-*CH*-(CH₂-O-CH₂-CH=CH₂)-O-), PAGE), 4.45-4.49 (s, -C₆H₆-*CH*₂-O-), 5.12-5.27 (m, -O-CH₂-CH-*CH*₂-, PAGE), 5.83-5.91 (m, -O-CH₂-*CH*-CH₂-, PAGE), 7.10-7.22 (br, m-, *p*-aromatic,-CH₂-C₆H₆-CH₃).



Figure S1. Representative ¹H NMR spectrum of synthesized PAGE in CDCl₃.

PS-b-PAGE: ¹H NMR (400 MHz, CDCl3, δ, ppm) = 0.53-0.78 (br, -CH(CH3)-CH2-CH3, 6H), 1.26-1.69 (br, backbone, -CH2-CH-, PS), 1.69-2.46 (br, backbone, -CH2-CH-, PS), 3.40-3.52 (m, -CH2-O-, 2H), 3.40-3.49 (m, -O-CH2-CH(OH)-CH2-O, PAGE), 3.96-3.98 (d, -CH2-CH-(CH2-O-CH2-CH=CH2)-O-), PAGE), 5.12-5.27 (m, -O-CH2-CH-CH2-, PAGE), 5.83-5.91 (m, -O-CH2-CH-CH2-, PAGE), 6.30-6.85 (br, o-aromatic, PS), 6.85-7.29 (br, m-, p-aromatic, PS)



Figure S2. Representative ¹H NMR spectrum of synthesized PS-*b*-PAGE in CDCl₃.

PS-b-PAGE(CH₃): ¹H NMR (400 MHz, CDCl₃, δ , ppm) = 0.88-0.93 (t, -S(CH₂)₃*CH*₃), 1.36-1.43 (br, -*CH*₂-CH- and -CH(*CH*₂)₄O- and -S(CH₂)₂-*CH*₂-CH₃), 1.43-1.60 (br, -CH₂-*CH*- and -CH₂-*CH*₂-S-), 2.47-2.58 (m, -O-CH₂-*CH*₂-S-*CH*₂-CH₂-), 3.40-3.70 (m, -*CH*₂-O- and -O-*CH*₂-*CH*(*CH*₂-O-*CH*₂-CH₂-S(CH₂)₃-CH₃)-O -), 6.30-6.85 (br, *o*-aromatic), 6.85-7.29 (br, m-, *p*-aromatic).

PS-b-PAGE(OH): ¹H NMR (400 MHz, CDCl₃, δ, ppm) = 1.61-2.20 (br, -CH₂-CH- and -CH₂-CH₂-CH₂-S-), 2.30-2.51 (m, -CH₂-CH₂-S-), 3.40-3.91 (m, -CH₂-O- and -O-CH₂-CH(CH₂-O-CH₂-CH₂-S(CH₂)₂-CH₂-OH)-O -), 6.30-6.82 (br, *o*-aromatic), 6.82-7.21 (br, m-, *p*-aromatic).

PS-b-PAGE(COOH): ¹H NMR (400 MHz, CDCl₃, δ, ppm) = 1.61-2.20 (br, -CH₂-*C*H- and -*CH*₂-CH₂-S-), 2.45-2.70 (m, -O-CH₂-*CH*₂-S-*CH*₂-CH₂-), 3.40-3.91 (m, -*CH*₂-O- and -O-*CH*₂-*CH*(*CH*₂-O-*CH*₂-CH₂-S(CH₂)₂-*CH*₂-OH)-O -), 6.30-6.82 (br, *o*-aromatic), 6.82-7.21 (br, m-, *p*-aromatic). ¹H-NMR (400MHz, DMSO-6*d*) 11.48-13.05 (br, -CO-*OH*).





Figure S3. Representative ¹H NMR spectrum of synthesized PS-*b*-PAGE(CH₃[100%]), PS-*b*-PAGE(OH[100%]), and PS-*b*-PAGE(COOH[100%]) in CDCl₃. And the PS-*b*-PAGE(COOH[100%]) in DMSO-6d.
 PAGE(COOH): ¹H NMR (400 MHz, DMSO-*d*6, δ, ppm) = 1.61-1.76 (m, -O-CH₂-CH₂-CH₂-S-), 2.34-2.52 (m, -O-CH₂-CH₂-CH₂-S), 2.56-2.68 (m, -S-CH₂-CH₂-COOH), 3.20-3.72 (br, -O-CH₂-CH(CH₂-O-CH₂-CH₂-CH₂-S-), 2.34-2.52 (m, -O-CH₂-CH₂-CH₂-S), 2.56-2.68 (m, -S-CH₂-CH₂-COOH), 3.20-3.72 (br, -O-CH₂-CH(CH₂-O-CH₂-CH₂-CH₂-S-), 2.34-2.52 (m, -O-CH₂-CH₂-CH₂-S), 2.56-2.68 (m, -S-CH₂-CH₂-COOH), 3.20-3.72 (br, -O-CH₂-CH(CH₂-O-CH₂-CH₂-S-), 2.34-2.52 (m, -O-CH₂-CH₂-S), 2.56-2.68 (m, -S-CH₂-CH₂-COOH), 3.20-3.72 (br, -O-CH₂-CH(CH₂-O-CH₂-CH₂-CH₂-S-CH₂-CH₂-COOH)-O-), 4.40 (s, Ph-CH₂-O-), 11.65-12.90 (br, -CO-OH).



Figure S4. Representative ¹H NMR spectrum of synthesized PS-*b*-PAGE(COOH) in DMSO-*6*d and in THF-*8*d. **PAGE(OH)_z:** ¹H NMR (400 MHz, CDCl₃, δ , ppm) = 1.83-1.93 (br, -CH₂-CH- and -CH₂-CH₂-CH₂-S-), 2.56-2.64 (m, -CH₂-CH₂-S-), 3.46-3.77 (m, -CH₂-O- and -O-CH₂-CH(CH₂-O-CH₂-CH₂-S(CH₂)₂-CH₂-OH)-O-).



Figure S5. Representative ¹H NMR spectrum of synthesized PS-*b*-PAGE(OH)_z in CDCl₃.

In this study various functional groups were introduced into polymer side-chains to control the microphase separated structure. Because of the absorption in the column during size exclusion chromatography (SEC) analysis, the molecular weight of block copolymer (BCP) can hardly be determined accurately. Therefore, the molecular weight of BCPs were calculated by the molecular weight of polystyrene block in THF using polystyrene standards, and the monomeric ratio of polystyrene block determined using 1H NMR spectroscopy. In addition, in the estimation of effective Flory-Huggins interaction parameter (χ_{eff}) the polydispersity is necessary. Therefore, the samples for the χ_{eff} estimation were measured by SEC, and the results are as followed.



Figure S6. SEC chromatograms of precursor PS₆₂-*b*-PAGE₄₂, PS₆₂-*b*-PAGE₄₂(OH) and PS₆₂-*b*-PAGE₄₂(COOH) (eluent, THF; flow rate, 1.0 mL min⁻¹). The methylation of carboxyl groups was performed as ref 3.



Figure S7. SEC chromatograms of precursor PS_{62} -b-PAGE₄₂(OH[z(%)]) (eluent, THF; flow rate, 1.0 mL min⁻¹). In the SEC curve of PS_{62} -b-PAGE₄₂(OH[29%]) sample with a concentration of 1 mg / mL, a small peak was observed in the high molecular weight part. After decrease the concentration to 0.2 mg / mL (THF) solvent the high molecular weight peak was hardly observed which indicate the high molecular weight peak was from micelle.



Figure S8. SEC chromatograms of precursor PS_{62} -*b*-PAGE₄₂(OH[29%]) with different concentration (eluent, THF; flow rate, 1.0 mL min⁻¹).

Table S1.	Characteristics	of sv	ynthesized	BCPs.

Entry	Sample	M _{n,BCP} ^a (kg mol⁻¹)	Ν	V _{PS} ^b	\mathcal{D}^d
1	PS ₆₂ -b-PAGE ₄₂	10.4	164	0.59	1.03
2	PS ₆₂ - <i>b</i> -PAGE ₄₂ (COOH[100%])	14.1	126	0.42	1.12
3	PS ₆₂ - <i>b</i> -PAGE ₄₂ (OH[100%])	13.6	129	0.50	1.05
4	PS ₆₂ - <i>b</i> -PAGE ₄₂ (OH[78%])	12.9	133	0.52	1.05
5	PS ₆₂ - <i>b</i> -PAGE ₄₂ (OH[29%])	11.3	150	0.57	1.05
6	PS ₆₂ - <i>b</i> -PAGE ₄₂ (OH[26%])	11.2	149	0.57	1.04

^aCalculated based on the $M_{n,PS}$ determined by SEC in THF using polystyrene standards, and from the monomeric ratio determined using ¹H NMR spectroscopy. ^bCalculated from the monomeric ratio determined by ¹H NMR spectroscopy. The density of the polymer was calculated based on the reported and measured densities at 25°C (1.05 g/cm³ for PS, 0.96 g/cm³ for PAGE, 1.06 g/cm³ for PAGE(CH₃[100%]), 1.21 g/cm³ for PAGE(COOH[100%])), and 1.19 g/cm³ for PAGE(OH[100%])). ^cDetermined by SEC in THF using polystyrene standards.

Thermal characteristics of synthesized BCPs

To investigate the thermal behavior of synthesized polymers, and to decide the annealing temperature, TG-DTA and DSC were performed. Glass transition temperatures (T_g) and the decomposition temperature were determined by DSC and TG-DTA, respectively.



Figure S9. Representative TG-DTA curves of Synthesized PS-OH.

Entry	Sample	$M_{n,BCP}^{a}$	V-b	TCLOCY	True d(°C)
Liftiy	Sample	(kg mol ⁻¹)	Vps	7g (C)	7 _{10%} (C)
1	PS ₂₁₁ (OH)	22.0	-	99	384
2	PS ₂₁₁ - <i>b</i> -PAGE ₁₄₇	38.8	0.54	84	358
3	PS ₂₁₁ - <i>b</i> -PAGE ₁₄₇ (CH ₃ [100%])	52.1	0.42	-	335
4	PS ₂₁₁ - <i>b</i> -PAGE ₁₄₇ (COOH[100%])	52.4	0.45	67	304
5	PS ₂₁₁ - <i>b</i> -PAGE ₁₄₇ (OH[100%])	52.4	0.45	69	309

Table S2. Characteristics of the Synthesized PS-*b*-PAGE.

^aCalculated based on the $M_{n,PS}$ determined by SEC in THF using polystyrene standards, and from the monomeric ratio determined using ¹H NMR spectroscopy. ^bCalculated from the monomeric ratio determined by ¹H NMR spectroscopy. The density of the polymer was calculated based on the reported and measured densities at 25°C (1.05 g/cm³ for PS, 0.96 g/cm³ for PAGE, 1.06 g/cm³ for PAGE(CH₃[100%]), 1.21 g/cm³ for PAGE(COOH[100%]), and 1.19 g/cm³ for PAGE(OH[100%])). ^cDetermined by DSC. ^dDetermined by and TG/DTA.

Estimation of the functional group introduction ratio: To compare the influence of the hydroxyl group contents on the self-assembly behavior, we synthesized PS-*b*-PAGE(OH)[z(%)], specimens (where *z* is the introduction ratio of hydroxyl group) containing different amounts of hydroxyl groups.

The introduction ratio z (%) was estimated by calculating the conversion of the PAGE vinyl groups using ¹H NMR spectroscopy. More specifically, the -O-CH₂-CH-CH₂- peak at 5.83-5.91, the *o*-aromatic proton peak at 6.30-6.82 and *p*-aromatic at 6.82-7.21, as follows:

$$z = \left(\frac{n_{hyd.}}{n_{vin.0}}\right) \times 100$$
$$= \left(\frac{n_{vin.loss}}{n_{vin.0}}\right) \times 100$$
$$= \left(\frac{n_{vin.0} - n_{vin.rem.}}{n_{vin.0}}\right) \times 100$$

where n_{hyd} is the number of moles of hydroxyl groups introduced, $n_{vin.0}$ is the number of the moles of vinyl groups before functionalization, $n_{vin.loss}$ is the modified mole number of moles of vinyl groups, and $n_{vin.rem.}$ is the remaining vinyl group after functionalization.

Since number of moles of phenyl groups remained unchanged during modification, then:

$$z = \left(\frac{\frac{n_{vin.0}}{n_{phe.0}} - \frac{n_{vin.rem}}{n_{phe.rem}}}{\frac{n_{vin.0}}{n_{phe.0}}}\right) \times 100$$

where $n_{phe.0}$ is the number of moles of phenyl groups before functionalization, and $n_{phe.rem.}$ is the number of moles of phenyl groups after functionalization. Thus:

$$z = \left(\frac{\frac{I_{vin.0}}{I_{phe.0}} - \frac{I_{vin.rem.}}{I_{phe.rem.}}}{\frac{I_{vin.0}}{5}}\right) \times 100$$
$$= \left(1 - \frac{I_{vin.rem.}}{I_{phe.rem.}} \cdot \frac{I_{phe.0}}{I_{ven.0}}\right) \times 100 (1)$$

where $I_{vin.0}$ represents the integrated area of vinyl groups from the ¹H NMR spectrum before functionalization and $I_{vin.rem.}$ represents the integrated area of vinyl groups after functionalization. Similarly, $I_{phe.0}$ and $I_{phe.rem.}$ represent the integrated area of phenyl groups from the ¹H NMR spectrum before and after functionalization, respectively.

The M_n of the prepared PS-*b*-PAGE(OH[z(%)]) was determined using SEC while the w_{PS} of the modified PS*b*-PAGE was obtained from the M_n of the functionalized BCP and the M_n of the PS block of the precursors. **Estimation of the normalized polymerization degree:** The degree of polymerization N was calculated by: $N = N_i + N_i$

where N_i and N_j are the degrees of polymerization of polymers i and polymer j, respectively:

$$N_i = \frac{v_i M_{n,i}}{v_0 F W_i}$$

where:

$$\nu_i = \frac{FW_i}{\rho_i N_A}$$

thus:

$$N_i = \frac{M_{n,i}}{\rho_i N_A \nu_0} (2)$$

where $M_{n,i}$ is the molecular weight of polymer i, ρ_i is the density of polymer i, N_A is Avogadro constant, and v_0 is the reference volume for normalization.

Density Estimation of post-functionalized PAGE: PAGE homopolymer was polymerized and post-functionalized with different hydroxyl group contains. Then the density of PAGE(OH[z(%)])s were estimated by density gradient tube method at 25 °C. A density gradient tube and a group contribution method^[1] was prepared by using 250 mL graduated cylinder filled. Density gradient liquid was prepared by using calcium iodide and water. The density of chemical reagents used, and their height of gravity center was read and summarized in Table S1. and Table S3. The height and density of reagents was plotted in Figure S5. and the equation of height (x) and density (y) was obtained to calculate the density of PAGE(OH[z(%)]) samples.

Table 55. Height in density gradient tabe and density of reference enemical agent.
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Reagent	Height (cm)	Density (g/cm ³)
Phenyl Ether	199	1.07
1-Bromooctane	164	1.11
1-Bromohexane	102	1.18
Nitrobenzene	80	1.20



Figure S10. Scale and density of chemical reagent.

The height of gravity center of polymer samples then was read, and their density was calculated by the equation above. The height (x) and density (y) were summarized in Table S2. and plotted in Figure S6. Then the equation of introduction ratio of hydroxyl groups (z) and density (y) was obtained.

Table S4. Height in density gradient tube and density o	f synthesized PAGE(OH[z(%)]).
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Sample	Height (cm)	Density (g/cm ³)
PAGE(OH[27%])	196	1.07
PAGE(OH[44%])	162	1.11
PAGE(OH[80%])	118	1.16
PAGE(OH[91%])	100	1.18



Figure S11. Scale and density of synthesized PAGE(OH[z(%)]).

By using the same method, the density of PAGE(COOH[100%]) was estimated to be 1.21 g/ml at the height of 158 cm in the density gradient tube.

Table S5. Height in density gradient tube and density of reference chemistry agent.

Reagent	Height (cm)	Density (g/cm ³)
1-Bromoocatane	226	1.11
1-Bromohexane	208	1.13
Nitrobenzene	167	1.20
1-2-dichloroethane	130	1.25



Figure S12. Scale and density of chemical reagent.

The density of PAGE, PAGE(CH₃[100%]), PAGE(OH[100%]), and PAGE(COOH[100%]) determined by different methods was summarized in Table S6.

Sample	Density (g/cm ³) ^[1]	Density (g/cm ³) ^a	Density (g/cm ³) ^b
PAGE	0.96	-	1.05
PAGE(CH ₃ [100%])	-	-	1.06
PAGE(OH[100%])	-	1.19	1.22
PAGE(COOH[100%])	-	1.21	1.28

^aDetermined based on the height by density gradient tube. ^bDetermined by group contribution method.

Small-Angle X-ray Scattering (SAXS)

Preparation and SAXS analysis of bulk sample: The bulk sample used to investigate were prepared by slowly evaporating a dilute BCP THF solution filtered through a 0.25 μ m pore size PTFE membrane syringe filter at room temperature. The annealing temperature was decided to be at 150 °C, which is 50 °C higher than the T_g of homopolymer PS-OH, homopolymer PAGE, and block copolymer, and lower than the $T_{5\%}$ of each polymer The asprepared samples were dried under reduced pressure before annealing at 150 °C for 24 h.

Preparation and SAXS analysis capillary sample: The capillary sample was used for estimation of Flory-Huggins interaction parameter by RPA method^[2]. The polymer sample was filled in a quartz glass capillary with a 1.5 mm outer diameter and 0.01 mm wall thickness. The polymer sample temperature for PS-*b*-PAGE was decreased from 295 to 250 centigrade. With a 5 degree Celsius decrement. The polymer sample temperature for PS-*b*-PAGE(OH[100%]) and PS-*b*-PAGE(COOH[100%]) were increased from 220 to 290 centigrade. With a 5 degree Celsius decrement.

Estimation of χ_{eff} by fitting the SAXS curves using RPA method: the BCPs were analyzed by SAXS over a range of temperature in the mean-field state and their scattering behavior was fitted using RPA method.

To calculate the χ_{eff} , the intensity (*I*) of the first order scattering peak was fitted using the following expression:

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

Where A_0 is constant, S(q) and W(q) are autocorrelation function, and χ_{eff} is the effective Flory-Huggins interaction parameter. Then:

$$S(q) = \langle S_{i,j} \rangle + 2\langle S_{i,j} \rangle + \langle S_{j,j} \rangle$$

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

$$\langle S_{i,i}(q) \rangle = r_{c}f_{i}^{2}g^{(2)}{}_{i}(q)$$

$$\langle S_{i,j}(q) \rangle = r_{c}f_{i}f_{j}g^{(1)}{}_{i}(q)g^{(1)}{}_{j}(q)$$

$$r_{c} = \frac{\left(v_{i}N_{i} + v_{j}N_{j}\right)}{\left(v_{i} \cdot v_{j}\right)^{\frac{1}{2}}}$$

$$v_{i} = \frac{FW_{i}}{\rho_{i}N_{A}}$$

$$N_{i} = \frac{v_{i}M_{n,i}}{v_{0}FW_{i}}$$

$$g^{(1)}{}_{i}(q) = \frac{1}{y_{i}(q)} \cdot \left\{1 - [y_{i}(q) \cdot (D_{i} - 1) + 1]^{-(D_{i} - 1)^{-1}}\right\}$$

$$g^{(2)}{}_{i}(q) = \frac{1}{y_{i}(q)^{2}} \cdot \left\{-1 + y_{i}(q) + [y_{i}(q) \cdot (D_{i} - 1) + 1]^{-(D_{i} - 1)^{-1}}\right\}$$

$$y_{i}(q) = \frac{N_{i}b_{i}^{2}}{6}q^{2}$$

$$D_{i} = \frac{\frac{M_{W}}{M_{n}} - 1}{w_{i}^{2} + w_{i}^{2}} + 1$$

Where, f_i is the volume fraction of polymer i, FW_i is the formula weight of monomer i, ρ_i is the density of polymer i, N_A is the Avogadro constant, $M_{n,i}$ is the number average molecular weight of polymer i, v_0 is the reference volume for normalization, b_i is the Kuhn length of polymer i, $N_i b_i^2$ is the radius of gyration of polymer i, $\frac{M_W}{M_n}$ is the polydispersity of BCPs, and w_i is the weight fraction of polymer i. The subscript i or j represent different kinds of segments. Then A_0 , b_i , b_j , and χ_{eff} were fitted.



Figure S13. Representative SAXS profile and fitting curve of PS-*b*-PAGE, PS-*b*-PAGE(OH[100%]), and PS-*b*-PAGE(COOH[100%]).

Estimation of order-disorder transition temperature (T_{ODT})**:** The full width at half maximum (FWHM) on the primary peak of the SAXS profile was calculated from the equation of Gaussian to fit the SAXS curves:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{\frac{-(x-\mu)^2}{2\sigma^2}}$$

Then the FWHM:

$$FWHM = 2\sqrt{2}ln\sigma$$



The T_{ODT} was confirmed by plotting the temperature verses the FWHM on the primary peak of the SAXS profile.

Figure S14. Temperature dependence of FWHM.

Table S7. T_{ODT} of Synthesized BCPs.

Sample	<i>Τ</i> _{ODT} (°C)
PS-b-PAGE	265
PS- <i>b</i> -PAGE(OH[100%])	253
PS-b-PAGE(COOH[100%])	260
PS-b-PAGE(OH[26%])	240
PS-b-PAGE(OH[29%])	234
PS- <i>b</i> -PAGE(OH[78%])	257



Figure S15. SAXS profiles of PS₃₇₅-b-PAGE₁₁₈ and PS₃₇₅-b-PAGE₁₁₈(CH₃[100%]).

Reference

- R. F. Fedors, *Polym. Eng. Sci.*, 1974, **14**, 147-154.
 S. Antoine, Z. Geng, E. S. Zofchak, M. Chwatko, G. H. Fredrickson, V. Ganesan, C. J. Hawker, N. A. Lynd, and R. A. Segalman, *Macromolecules*, 2021, **54**, 6670-6677.
- [3] M. Jacquin, P. Muller, R.Talingting-Pabalan. H. Cottet, J. F. Berret, T. Futterer, O. Theodoly, J. Colloid Interface Sci, 2007, 361, 897-911.