Electronic Supplementary Information

An Experimental and Theoretical Investigation into the Self-assembly of a Chemically Modified High-χ Coil-rod Diblock Copolymer

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Synthesis of homopolymer homo-PMVS

In a 30 mL Schlenk flask 15 mL dehydrated tetrahydrofuran (THF) without stabilizer was added under Ar protection. To remove the moisture and oxygen dissolved in THF, after being cooled down to -78°C, roughly 0.2 ml *sec*-BuLi (in 1.04 M hexane/cyclohexane solution) was added with THF solution color changing from transparent to yellow. Afterwards, Schlenk flask was kept under room temperature till the previous yellow color vanished, indicating that *sec*-BuLi in solution became inactive. Again, Schlenk flask was cooled down to -78°C, 0.200 mL *sec*-BuLi (0.003 g, 0.208 mmol in 1.04 M cyclohexane solution) was added as the initiator of the anionic polymerization. Subsequently, a calculated amount of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D3v) monomers (2.0 g, 7.75 mmol) was added into the reactor. After 10 min, the reaction temperature was increased to -20°C. Excessive TMSiCl was added into the reactor after 24 hr and the resulting polymer was precipitated in methanol. A transparent viscous liquid was obtained.

¹H NMR(CDCl₃, 400MHz) δ(ppm): 0.14 (s, 3H, CH₃), 5.76-6.04 (br, 3H, CH=CH₂).

Synthesis of homopolymer homo-PSi8F

In a 10 mL recovery flask, 0.10 g synthesized homo-PMVS (1.16 mmol MVS units), 1.67 g 1H,1H,2H,2H-perfluorodecanethiol (3.0 mole equiv. to MVS repeating units) and 28.6 mg Azobisisobutyronitrile (AIBN) (0.15 mole equiv. to MVS repeating units) were added to degased 2.0 mL THF. The solution was stirred at 65°C for 5 hr under Ar atmosphere. Afterwards, the flask was soaked in liquid N_2 for termination of reaction. A chunk of white solid was precipitated after the reaction. The insoluble solid was repeatedly washed with THF and dried in vacuo under 40°C overnight to yield the product.

Homopolymer	M_n (kg mol ⁻¹)	Đ	$T_g(^{\mathrm{o}}\mathrm{C})$	$T_{iso}(^{\mathrm{o}}\mathrm{C})$
Homo-PMVS	9900	1.54	-	-
Homo-PSi8F	insoluble	insoluble	<-30	53.5



 Table S1. Characteristics of the synthesized homopolymers.

Fig. S1. ¹H NMR spectra of synthesized homo-PMVS in CDCl₃ solvent.



Fig. S2 (a). ¹H NMR spectras of synthesized (a) PS-*b*-PMVSs and (b) PS-*b*-PSi8Fs in CDCl₃ solvent.



Fig. S2 (b). ¹H NMR spectras and peak integration results of synthesized PS-*b*-PSi8F (SF 20.8) in CDCl₃ solvent.



Fig. S3. SEC chromatography of precursor PS-*b*-PMVS (SV) and corresponding PS*b*-PSi8F (SF) after post-functionalization.



Fig. S4. DSC curves of the studied PS-*b*-PSi8Fs and homo- PSi8F at a heating rate of 10 °C /min under nitrogen atmosphere.

Homopolymer	C.A.(H ₂ O) ^a (°)	C.A.(CH ₂ I ₂) ^a (°)	Dispersive (mJ m ⁻²)	Polar (mJ m ⁻²)	SFE ^b (mJ m ⁻²)
PSi8F	125.6 ± 1.1	108.6 ± 1.3	5.6	0.3	5.9
PS ^c	-	-	34.5	6.1	40.7

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

^a Average values of measurements taken at 5 positions. ^b Calculated by the Owens-Wendt method¹. ^c The SFE of PS was obtained from the reference² as PS was partially soluble in diiodomethane.



Fig. S5. SAXS profiles of the as-prepared chemically modified PS-*b*-PSi8F bulk samples. The green triangle indicates the scattering peak attributed to the LC structure of perfluoroalkyl side chain.



Fig. S6 TEM micrograph of SF20.8 bulk sample showing the different grains consisted of hexagonally packed PSi8F cylinder domains aligned perpendicular (outplane) or parallel (in-plane) to the screen, as rapidly cooled from 180 °C annealing temperature to room temperature. The dark and bright domains are corresponding to PS and PSi8F segments, respectively, due to selective ruthenium tetraoxide staining of the PS segments.

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, 1.01 g cm⁻³ for PMVS and 1.65 g cm⁻³ for PSi8F, v_X is the molar volume of X. N_X is the degree of polymerization normalized over a common reference volume ($v_0 = 118 \text{ Å}^3$) for X, FW is the formula weight of X, $N_{\rm A}$ is Avogadro's constant, and $b_{\rm X}$ is the segmental length of X. Here we assumed the dispersities for each homopolymer segment (D_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 at varied temperatures were summarized in Table S3.

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

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

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

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

$$r_{c} = \frac{(v_{PS}N_{PS} + v_{Y}N_{Y})}{(v_{PS} \cdot v_{Y})^{1/2}} \quad v_{X} = \frac{FW_{X}}{\rho_{X}N_{A}} \quad N_{X} = \frac{v_{X}M_{n,X}}{v_{0}FW_{X}}$$

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

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

$$y_X(q) = \frac{N_X b_X^2}{6} q^2$$
 $D \equiv D_{PS} = D_Y = \frac{M_w / M_n - 1}{w_{PS}^2 + w_Y^2} + 1$

X = PS or Y(Y = PMVS or PSi8F).

Table S3. The fixed parameters used to estimate χ_{eff} for PS-*b*-PMVS (SF6.7) and PS-*b*-PSi8F (SF5.8).

ВСР		M _n	$M_{ m w}$	M _{n,PS}	f	141
	I _c	(kg mol ⁻¹)	(kg mol ⁻¹)	$(kg mol^{-1})$	JPS	WPS
PS- <i>b</i> -PMVS	02	67	76	37	0.55	0.56
(SV6.7))2	0.7	7.0	5.7	0.55	0.50
PS-b-PSi8F	61	5 0	7 4	2.6	0.72	0.62
(SF5.8)	01	5.8	/.4	5.0	0.72	0.02

	Estimated χ_{eff}		Estimated χ_{eff}
<i>T</i> (°C)	PS-b-PMVS	T (° C)	PS- <i>b</i> -PSi8F
	(SV6.7)	$T(\mathbf{C})$	(SF5.8)
160	0.09500	240	0.16814
170	0.09482	250	0.16806
180	0.09488	260	0.16798
190	0.09483	270	0.16789
200	0.09478	280	0.16779
210	0.09467	290	0.16769
220	0.09478		
230	0.09462		
240	0.09448		

Table S4. The fixed parameters used to estimate χ_{eff} for PS-*b*-PMVS (SF6.7) and PS*b*-PSi8F (SF5.8).



Fig. S7. (a) The scattering profiles measured by SAXS in scatters at 160-240 °C and fitted curves at 160-240 °C and (b) $I_{\text{max}}^{-1}-T^{-1}$ plots for PS-*b*-PMVS (SF6.7) and (c) estimated χ parameter– T^{-1} plots for PS-*b*-PMVS (SF6.7).



Fig. S8. (a) The scattering profiles measured by SAXS in scatters at 290-220°C and fitted curves at 290-250°C and (b) $I_{\text{max}}^{-1}-T^{-1}$ plots for PS-*b*-PSi8F (SF5.8) and (c) estimated χ parameter– T^{-1} plots for PS-*b*-PSi8F (SF5.8).



Fig. S9. The predicted 2-D morphologies calculated using SCFT for (a) SF 20.8, (b) SF 7.2, (c) SF 6.0 and (d) SF 5.8 using the assumptions of equal segments length (a=1; b=1). The red and blue colors indicate PS and PSi8F segments in left column and invert in right column. The density gradient bar for different segments is given next to each image.



Fig. S10. The in-situ evolution of 2-D morphologies calculated using SCFT for SF 20.8 using the assumptions of varied segments length (a=1; b=2.3) after running for (a) 17 steps; (b) 22 steps; (c) 33 steps; (d) 45 steps; (e) 64 steps; (f) 86 steps; (g) 195 steps; (h) 1003 steps. The red and blue colors indicate PS and PSi8F segments in left column and invert in right column. The density gradient bar for different segments is given next to each image.

Reference

- 1. D. K. Owens and R. Wendt, J. Appl. Polym. Sci., 1969, 13, 1741-1747.
- 2. S. Wu, J. Phys. Chem., 1970, 74, 632-638.