**Supporting Information**

# Morphology Transitions of Linear $A_1B_1A_2B_2$ Tetrablock Copolymers at Symmetric Overall Volume Fraction

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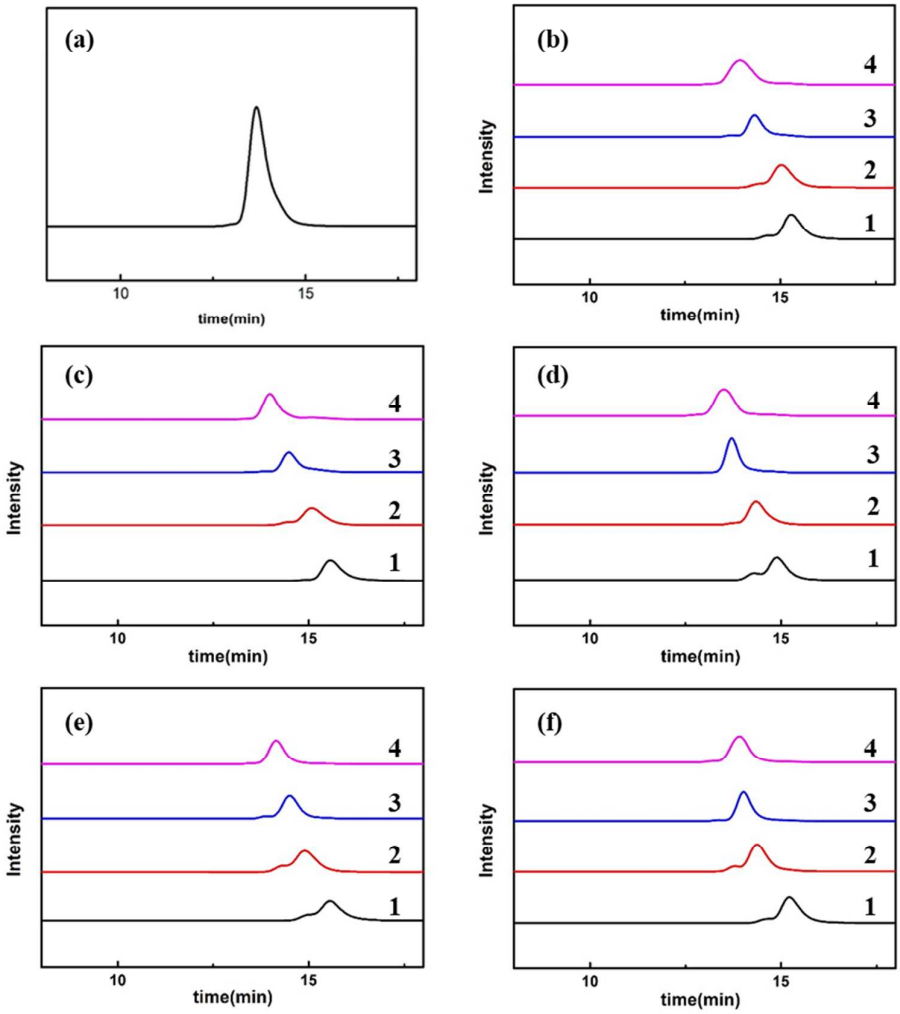


**Figure S1.** SEC traces of (a) SISI0, (b) SISI17, (c) SISI24, (d) SISI30, (e) SISI40, (f) SISI60. 1: $S_1$, 2: $S_1I_1$, 3: $S_1I_1S_2$, 4: $S_1I_1S_2I_2$.

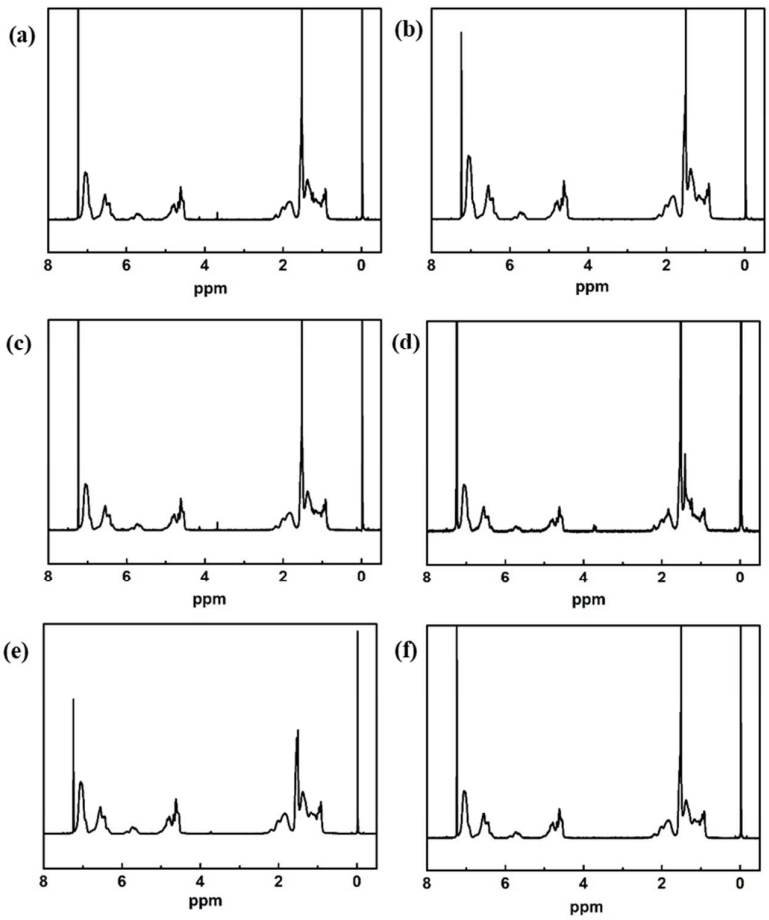


**Figure S2.** $^{1}$H NMR spectra of (a) SISI0, (b) SISI17, (c) SISI24, (d) SISI30, (e) SISI40, (f) SISI60.

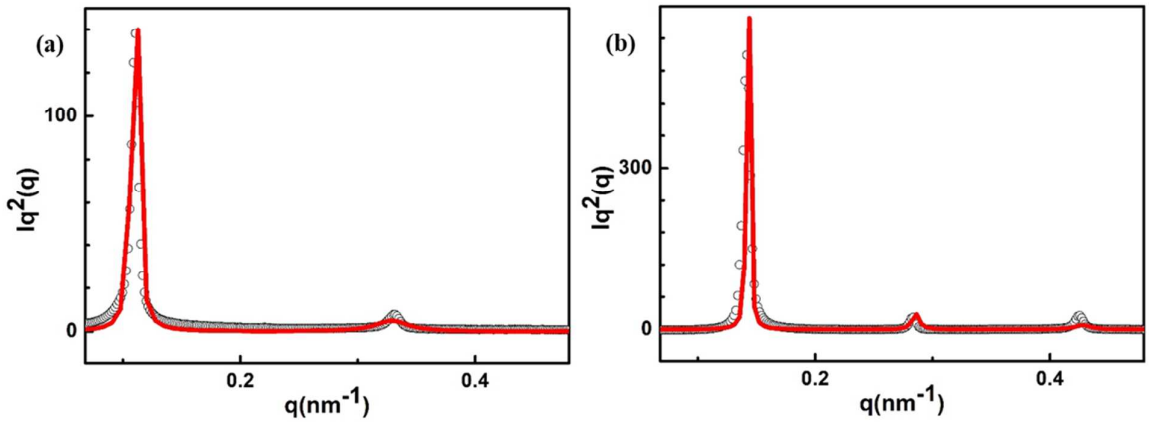


**Figure S3.** Curve-fitted SAXS profiles by variable lamellar thickness model (line) and experimental SAXS profiles (dot) for (a) SISI0 and (b) SISI17. The details of the calculation are referred to previous paper.[1] The predicted volume fraction of PS in SISI0 and SISI17 from the best fit SAXS profiles is 0.51 and 0.59, respectively.

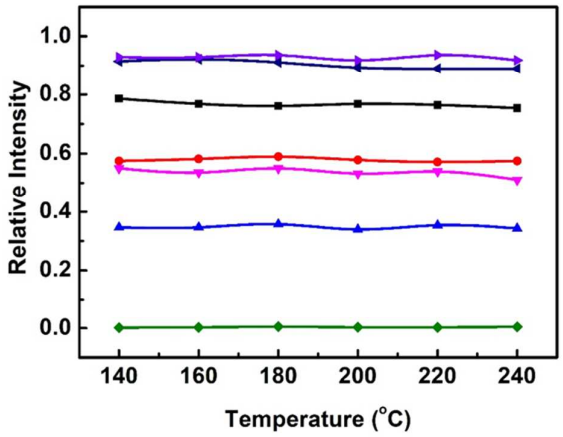


**Figure S4.** Plot of depolarized light scattering intensity versus temperature for all $S_1I_1S_2I_2$ samples. Purple: SISI60, dark blue: SISI40, black: SISI0, red: SISI17, pink: SISI30, blue: SISI24, green: SISI34. All samples except SISI34 showed definite birefringence resulting from the ordered microdomains up to 240 $^{o}$C. The absence of birefringence indicates that a block copolymer has double gyroid and spherical microdomains as well as the disordered state. From TEM image and Figure S4, SISI34 has gyroid microdomains.

Table S1. Parameters of experimental SISI samples used in the calculations of SCFT.

| Sample | $f_{PI}$ | $\tau_{PI}$ | $\chi N$ |
|---|---|---|---|
| SISI0 | 0.49 | 0 | 59.8 |
| SISI17 | 0.46 | 0.17 | 48.2 |
| SISI24 | 0.49 | 0.24 | 55.1 |
| SISI30 | 0.46 | 0.3 | 65.5 |
| SISI34 | 0.49 | 0.34 | 55.1 |
| SISI40 | 0.49 | 0.4 | 41.7 |
| SISI60 | 0.48 | 0.6 | 51.0 |

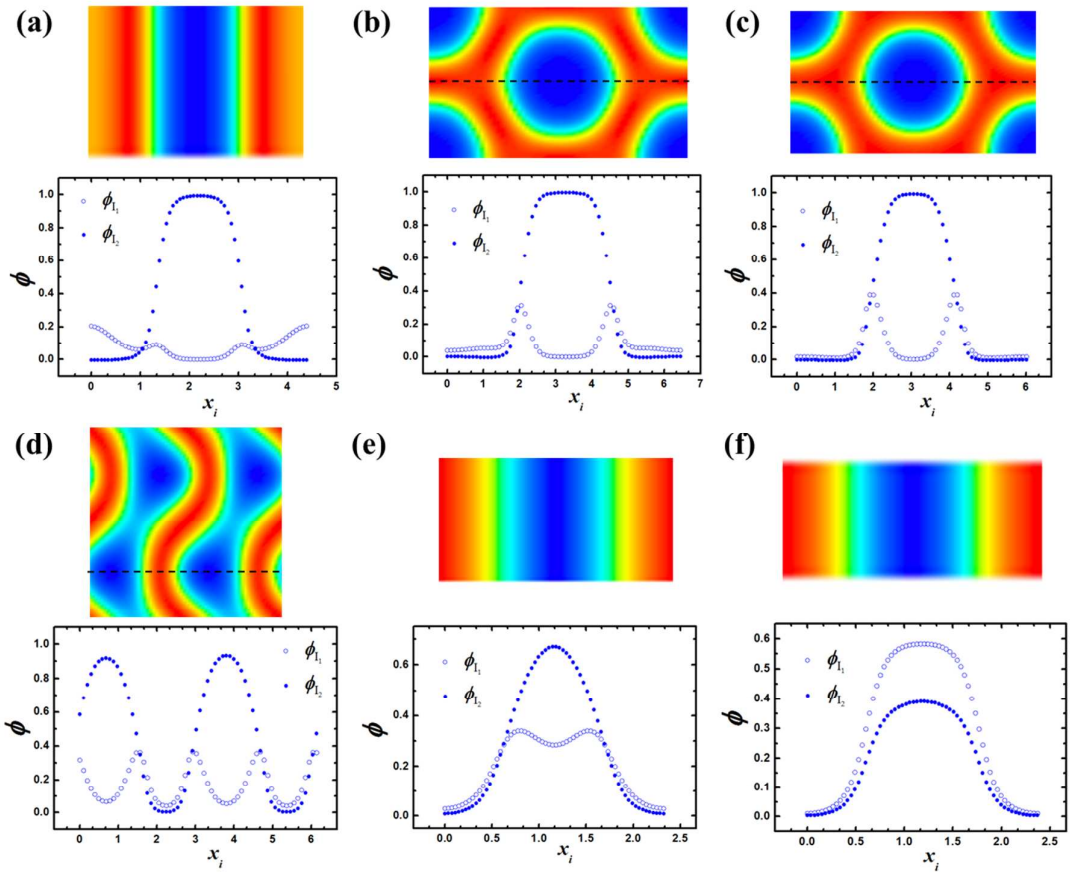


**Figure S5.** Density color maps and one-dimensional density distribution of $PI_1$ (open symbols) and $PI_2$ (filled symbols) chains in lamellar morphologies or cylindrical/gyroid morphologies along the direction indicated by the dashed lines for each sample. Blue and red represent PI and PS, respectively. (a) SISI17, (b) SISI24, (c) SISI30, (d) SISI34, (e) SISI40, (f) SISI60.

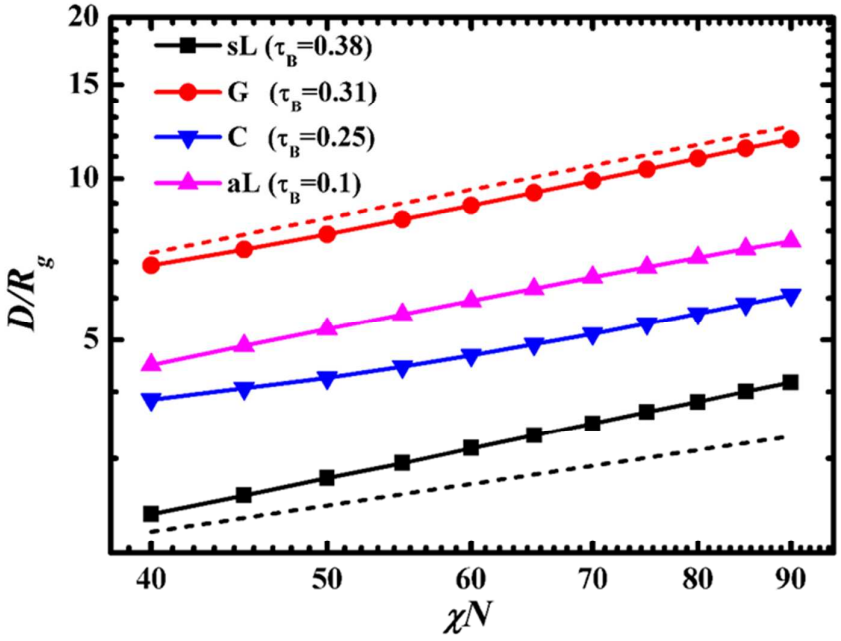


**Figure S6.** Domain spacing $D$ as a function of $\chi N$, for four different $A_1B_1A_2B_2$ tetrablock copolymers at fixed overall $f_A = f_B = 0.5$, $\tau_A = f_{A1}/f_{A,total} = 0.5$, but with different values of $\tau_B = f_{B1}/f_{B,total}$ = 0.1 (aL), 0.25 ($C_{PI}$), 0.31 ($G_{PI}$) and 0.38 (sL). The spatial unit is chosen as the radius of gyration ($R_g$) of an unperturbed polymer with the same length as the tetrablock copolymer at $\chi N$=40. It is assumed that the value of $\chi$ is fixed as constant so that the change of $\chi N$ is induced by the change of $N$. The red dashed line indicates the scaling relationship of $D \propto N^{2/3}$, while the black one indicates the scaling relationship of $D \propto N^{1/2}$. Interestingly, the change of D of all samples follows the relationship of $D \propto N^{2/3}$.

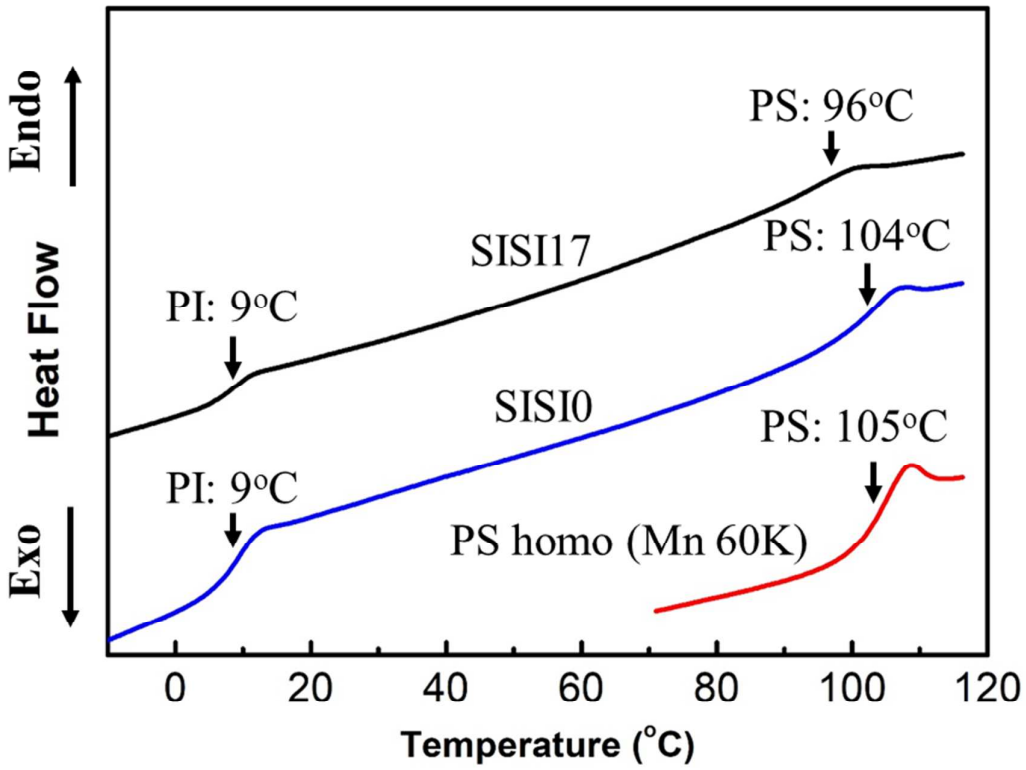


**Figure S7.** DSC curves obtained during the second heating run at a rate of 10 °C/min for PS homopolymer with a molecular weight of 60000, SISI0, and SISI17. Because PI was synthesized in THF solution, giving low 1,4 addition (< 10%), Tg of PI block was consistent to the value (~6 °C) reported in the literature.[2]

**References**

1. Kwak, J.; Han, S. H.; Moon, H. C.; Kim, J. K.; Koo, J.; Lee, J.-S.; Pryamitsyn, V.; Ganesan, V., Phase Behavior of Binary Blend Consisting of Asymmetric Polystyrene-block-poly (2-vinylpyridine) Copolymer and Asymmetric Deuterated Polystyrene-block-poly (4-hydroxystyrene) Copolymer. *Macromolecules* **2015,** *48* (4), 1262-1266.
2. Johnny, D. M. I.; Hsu, W.-L.; Halasa, A. F.; Sandstrom, P. H., Tire tread compound made with strain crystallizable 3, 4-polyisoprene. US Patent 5,356,997, 1994.