

Supporting Information

Asymmetric Double Tetragonal Domain Packing
from ABC Triblock Terpolymer Blends with Chain Length Difference

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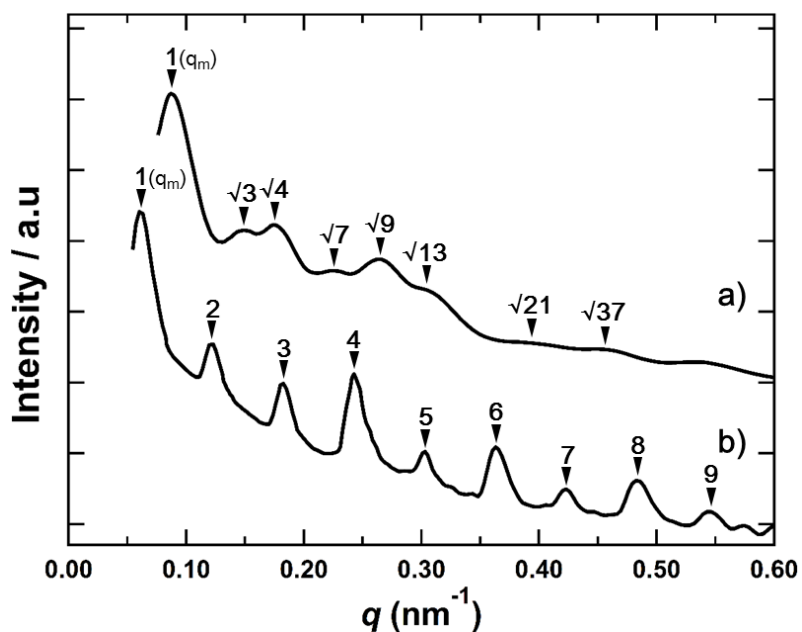


Figure S1. Azimuthally integrated SAXS diffraction patterns of the two parent ISP triblock terpolymers; (a) ISP-X and (b) ISP-Y. The black inverted triangles indicate the relative peak positions.

Figure S1 shows SAXS results of ISP-X and ISP-Y. The profile of ISP-X is a typical pattern for hexagonally packed structure, while that of ISP-Y is the one for a lamellar structure. D-spacing of ISP-X calculated from the primary peak ($q_m = 0.087 \text{ nm}^{-1}$) is 83 nm, which agrees well with the corresponding TEM result. On the other hand, the lamellar domain distance for ISP-Y is calculated to be 104 nm ($q_m = 0.060 \text{ nm}^{-1}$), which correspond reasonably with the value from the TEM image.

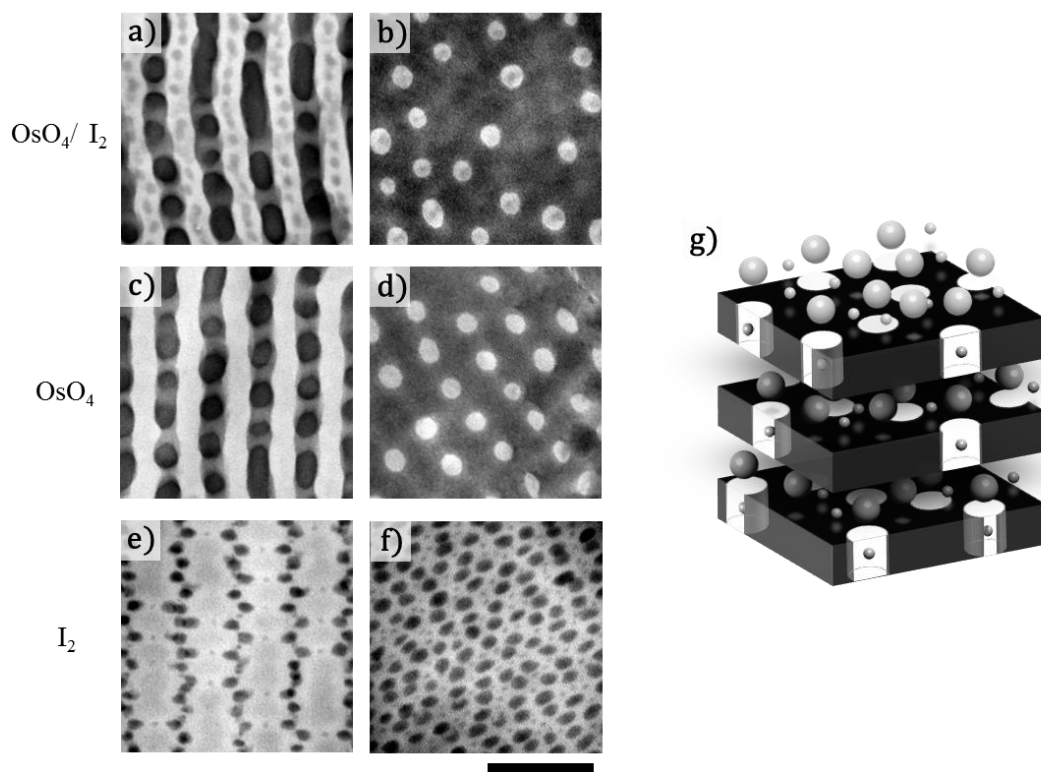


Figure S2. TEM images of Blend(2/8); staining agent for (a) and (b) is OsO_4/I_2 , that for (c) and (d) is OsO_4 , while that for (e) and (f) is I_2 . The images (a), (c) and (e) are taken parallel to the lamellar phase, whereas the images (b), (d) and (f) are shot perpendicular to the perforated lamellae. The scale bar represents 200 nm. (g) is a schematic representation of the current morphology, in which black and gray domain represent I and P phase, respectively.

Figure S2 compares the TEM images of Blend(2/8) stained with different staining reagents and observed from different directions. Forming perforated lamellae of I component was manifested by Figure S2(c) and (d). Figure S2(a) confirms the alignment of P spheres within S phase. Figure

S2(e) and (f) reveal that P phase consists of small and large spherical domains, both of which are distributed under regulation, particularly some small P sphere are located at the mid of I lamellae. By comparing Figure S2(b) with S2(d), we can also notice the presence of some P spheres in the holes of I phase. That is, P spheres are always distributed in S matrix, in which small and large P spheres are located in between I perforated phases, while some small P spheres are placed in the holes of I perforated phases. Figure S2(g) represent the schematic illustration of the perforated morphology.

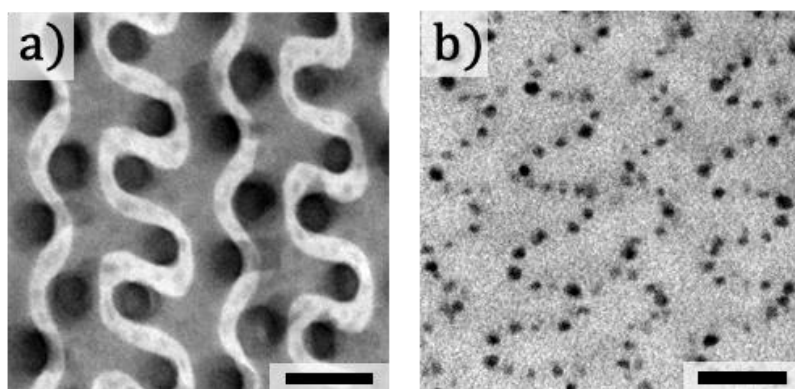


Figure S3. TEM images of Blend(1/9); (a) stained with OsO_4/I_2 and (b) stained with I_2 . Both images represent the projections of a double gyroid structure through the [112] plane. Two scale bars represent 100 nm.

Figure S3 shows the TEM images of Blend(1/9) stained with different reagents. Figure S3 (a) corresponds well to the [112] projection of a double gyroid structure. Although the double gyroid structure is composed of three components from ISP triblock terpolymers, the ordered bicontinuous double gyroid is developed, in which I component forms two gyroid networks in an S matrix. By comparing Figure S3 (a) with Figure S3 (b), P spherical domains can be confirmed to be lie on the S matrix. Considering the geometry of a double gyroid structure, the P spheres could be aligned on the gyroid triply periodic minimal surface or close.

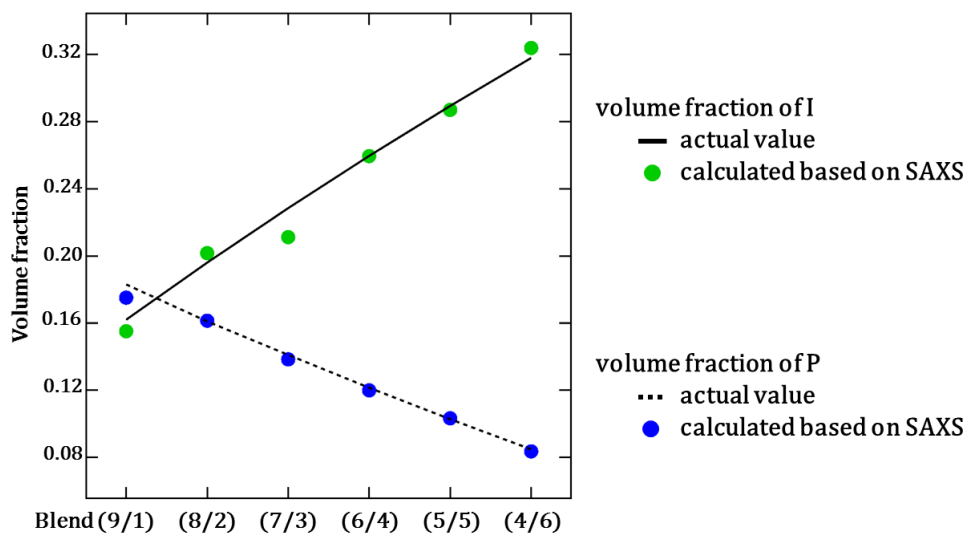


Figure S4. Volume fraction plots of various blends based on Table 2 and Table 3. Solid and dashed line indicate the exact volume fractions of I and P component according to Table 2, respectively. The volume fractions of I and P phases estimated from SAXS results are identified as green and blue circles.

Figure S4 shows the plot of various blends vs volume fraction of I and P components based on Table 2 and Table 3. The calculation results assuming all the I and P domains are cylinders are plotted as green and blue circles. Both circles are nearly on the lines of actual volume fraction of blend samples, which clearly indicates the volume fractions estimated from the calculation results match well with the exact volume fractions of the blend samples.

Calculation of scattering intensities of cylindrical structures

We calculated the structure factor $F(q)$ related to lattice structures in the scattering intensity $I(q)$ considering the absolute size of cylinders. The scattering intensity $I(q)$ can be expressed as

$$I(q) \propto |F(q)|^2 \quad (1)$$

$F(q)$ is referred as the structure factor

$$F(q) = \sum_j f_j \exp(-iq \cdot r_j) \quad (2)$$

$$f_j = \rho_{ej} f'_j \quad (3)$$

where j is the number of a scattering element in the unit cell, r_j is the j th domain position, f'_j is the form factor and ρ_{ej} is the electron density.

The expression of the form factor of cylindrical domain of radius R and length H is

$$f'_j = \int_0^{\pi/2} \left\{ \left[\frac{2J_1(qR \sin \varphi)}{qR \sin \varphi} \right] \left[\frac{\sin\left(\frac{qH}{2}\right) \cos \varphi}{\left(\frac{qH}{2}\right) \cos \varphi} \right] \right\}^2 \sin \varphi d\varphi \quad (4)$$

where $J_1(x)$ is the first order Bessel function. φ is defined as the angle between cylinder axis and the scattering vector, q . The integral over φ averages the form factor over all possible orientations of the cylinder with respect to q . Applying the microdomain structures of ABC triblock terpolymer to Eq 2 leads to the following equation,

$$F(q) = \sum f_A \exp(-iq \cdot r_{jA}) + \sum f_B \exp(-iq \cdot r_{jB}) + \sum f_C \exp(-iq \cdot r_{jC}) \quad (5)$$

Therefore, we can rewrite Eq 5 as an equation considering the difference between the electron densities of A or C domains and that of B matrix domain

$$F(q) = \Delta\rho_{eAB}f'_A \sum \exp(-iq \cdot r_{jA}) + \Delta\rho_{eCB}f'_C \sum \exp(-iq \cdot r_{jC}) + \rho_{eB}\{f'_A \sum \exp(-iq \cdot r_{jA}) + f'_B \sum \exp(-iq \cdot r_{jB}) + f'_C \sum \exp(-iq \cdot r_{jC})\} \quad (6)$$

where $\Delta\rho_{eAB} = \rho_{eA} - \rho_{eB}$ and $\Delta\rho_{eCB} = \rho_{eC} - \rho_{eB}$. We can neglect the third term regarding the scattering from B matrix domain because the term explains the structure factor from a unit lattice with the uniform electron density of ρ_{eB} . The structure factor can be expressed with Miller index of the diffraction lattice face (hkl) as $F(hkl)$,

$$F(hkl) = \Delta\rho_{eAB}f'_A \sum \exp[-2\pi i(x_{jA}h + y_{jA}k + z_{jA}l)] + \Delta\rho_{eCB}f'_C \sum \exp[-2\pi i(x_{jC}h + y_{jC}k + z_{jC}l)] \quad (7)$$

where (x_j, y_j, z_j) are the coordinates of the j th scattering element. In the case of ISP triblock terpolymer system (ρ_{eI} :0.512 electron/cm³, ρ_{eS} :0.565 electron/cm³, ρ_{eP} :0.608 electron/cm³), $\Delta\rho_{eIS} = -0.053$ electron/cm³ and $\Delta\rho_{ePS} = 0.043$ electron/cm³, we did use $\Delta\rho_{eIS} \neq -\Delta\rho_{ePS}$ to obtain the more accurate scattering intensity unlike our previous work.¹ In the present work, we can neglect l because cylindrical structure is a two-dimensional crystal.

References

1. Mogi, Y.; Nomura, M.; Kotsuji, H.; Ohnishi, K.; Matsushita, Y.; Noda, I. Superlattice Structures in Morphologies of the ABC Triblock Copolymers. *Macromolecules* **1994**, *27*, 6755-6760.