Supporting Information

Gyroid structures at highly asymmetric volume fractions by blending of ABC triblock terpolymer and AB diblock copolymer

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1. Characterization of neat block polymers

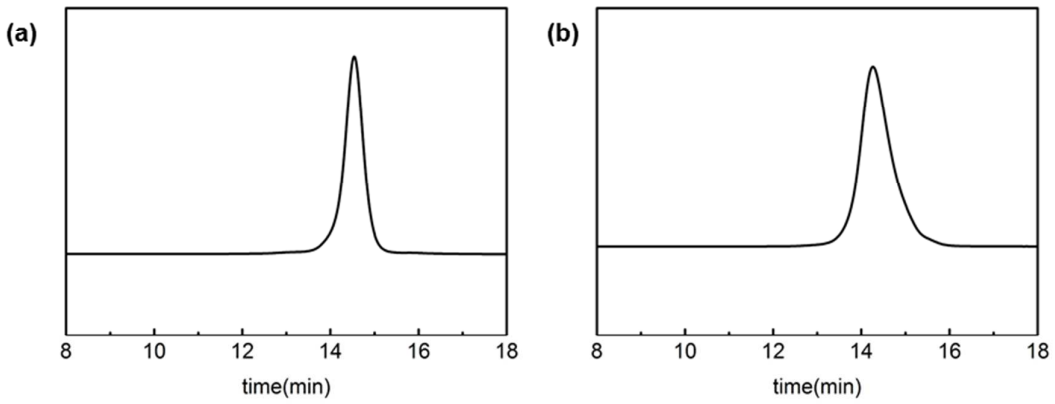

Figure S1. GPC traces of (a) PI-*b*-PS, and (b) PI-*b*-PS-*b*-P2VP

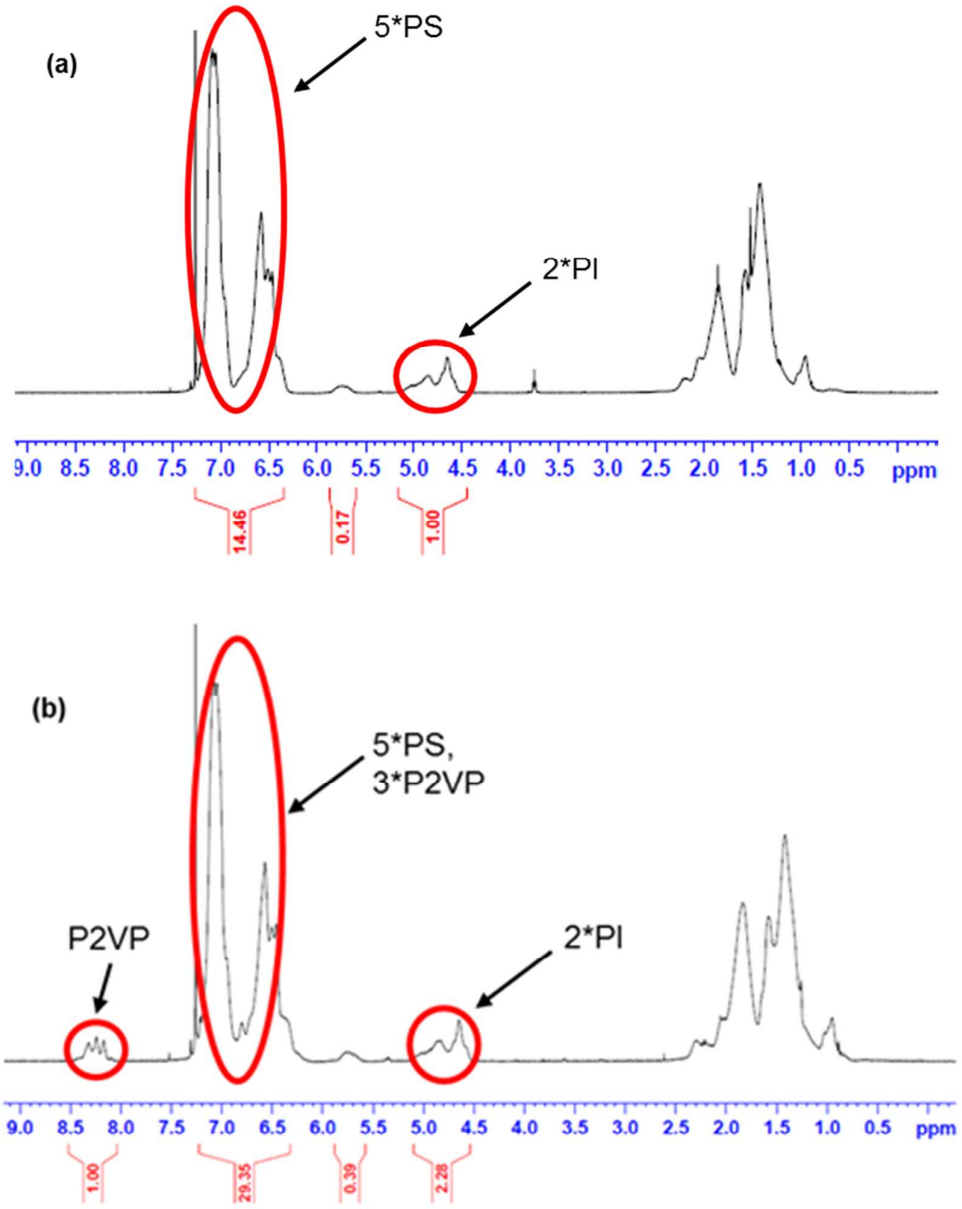

Figure S2. ^{1}H NMR spectra of (a) PI-*b*-PS, and (b) PI-*b*-PS-*b*-P2VP

2. SAXS profiles and TEM image of neat IS diblock copolymer

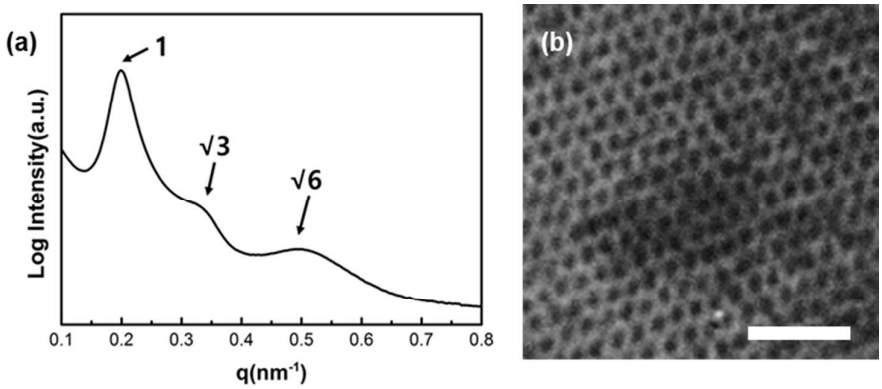

Figure S3. SAXS profile (a) and TEM image (b) of neat IS. Scare bar is 100 nm.

Figures S3a and S3b show SAXS profile and TEM image for neat IS. The SAXS profile shows scattering peaks at position of 1:√3:√6 relative to q*, indicating that neat IS shows body-centered cubic (BCC) spherical morphology. The dark regions in TEM image depict PI microdomains due to selective staining of PI by OsO_4.

3. TEM images of binary blend sample

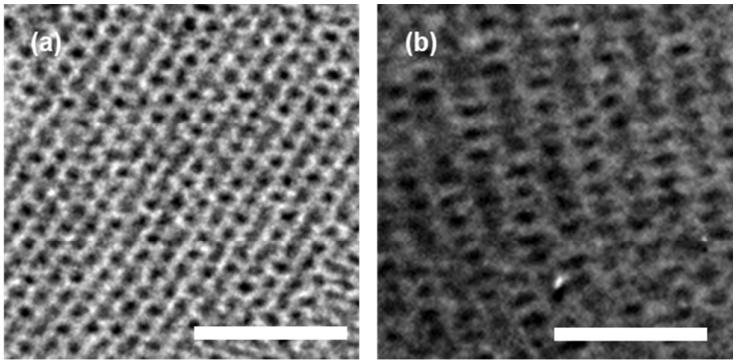

Figure S4. TEM images of blend samples (a) ISP75, (b) ISP50, showing gyroid structures [1 1 1] projection. TEM images were obtained after staining the samples with OsO_4. Scale bar is 100 nm.

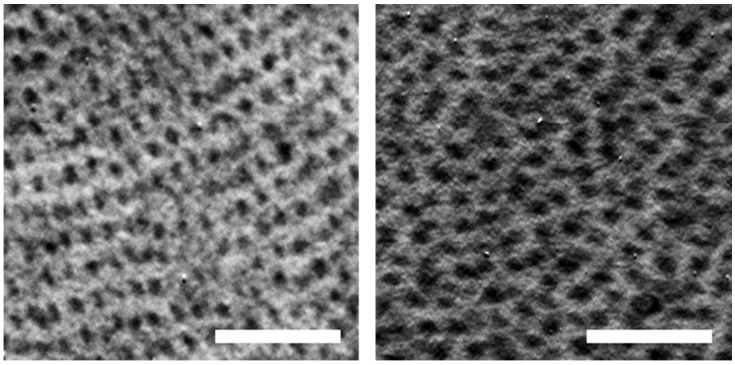

Figure S5. TEM images of blend samples (a) ISP33, (b) ISP25, showing spherical morphologies. TEM images were obtained after staining the samples with OsO_4. Scale bar is 100 nm.

4. Estimation of χ of PI and P2VP evaluated from the absolute SAXS intensities

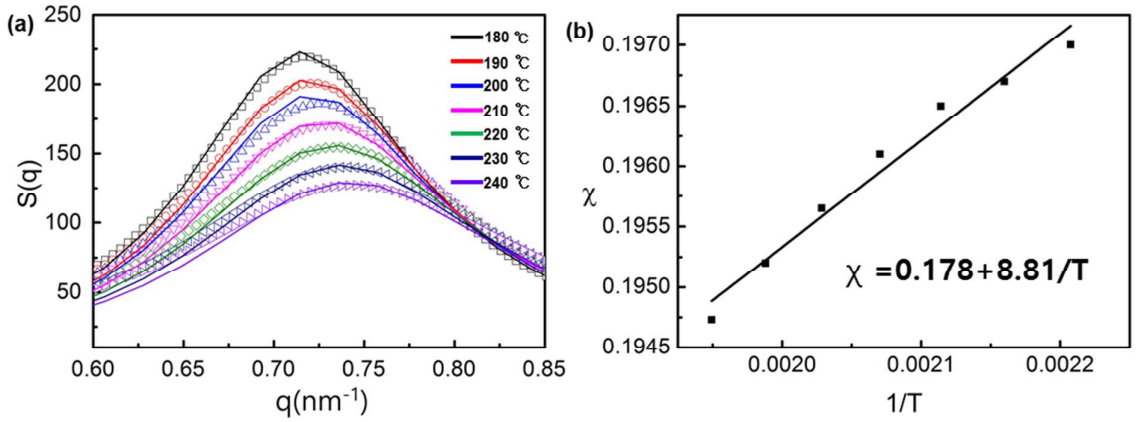

Figure S6. (a) Structure factors S(q) for symmetric PI-*b*-P2VP in disordered states at various temperatures (°C): 180, 190, 200, 210, 220, 230, 240. Symbols are experimental data and each solid line was obtained by curve-fitting SAXS profiles to the Leibler theory. (b) Plots of χ vs 1/T obtained from PI-*b*-P2VP.

Figure S6 gives the structure factor S(q), which was obtained from the absolute SAXS intensities of symmetric PI-*b*-P2VP (M_n = 4000 g/mol, f_I = 0.50), at various temperatures. Due to the broad correlation peak, this block copolymer becomes the disordered state at the entire experimental temperatures. The χ at various temperatures was obtained from the curve fitting of SAXS intensity to the Leibler theory.[1] The details of the calculation of χ are referred to previous papers.[2-3]

5. TEM and SAXS simulations

Gyroid modelling

For TEM and SAXS simulation, a gyroid model was generated with an assumption that the cocontinuous structure possesses the tricontinuous nature in which I/S and S/P interfaces are created by the pseudo parallel shift of the three-dimensional periodic minimal G surface. We followed exactly the procedures described by Suzuki et al.[4] The model that we built consisted of a unit cell of 100x100x100 voxels with three different electron densities corresponding to I, S, and P blocks for SAXS.

TEM simulation

We set the values of voxels with relative linear absorption coefficients, of which value was either 0 or 0.07 for non-stained and stained materials. Then the voxels are rotated according to a crystallographic direction of interest. Projection onto a square XY plane (-60 nm < X < 50 nm and -60 nm < Y < 50 nm) is performed for 40 nm thick film. Along the projection direction for a given pixel of XY plane, the coefficients of voxels located in the way are added to give a projected value $\mu(x, y)$ for a given pixel *xy*. Brightness of the projected image is then calculated using

$$I(x, y) = e^{-\mu(x,y)t}$$

SAXS simulation

Integrated diffraction intensity for a given Miller index was computed from the model as follows.

$$I(q_{hkl}) = \left| \sum_{i=1}^{N_{voxel}} \rho_i e^{-jq_{hkl} \cdot r_i} \right|^2$$

where ρ_i and r_i are electron density and position vector of a voxel *i*. N_{voxel} is the number of voxels and was taken as10^6 in this work. q_{hkl} is a scattering vector of a miller index (*h, k, l*). Intensities are calculated for all indices of a family of *hkl*, summed, and corrected for Lorentz factor $1/q_{hkl}^2$. Pseudo-Voigt function was used as a peak shape function of which

breadth was calculated with appropriate Debye Waller factor, domain size and microstrain values that best fit the experimental data.[5] For domain size, micro-strain, Debye Waller factor, and wavelength, 800 nm, 0.01, 4 nm, and 1Å were used, respectively. Finally, diffuse scattering with a form of $c/q^{3.5}$, were c is a scaling constant, was added to the sum of the peak functions for all diffraction peaks.[6]

References

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