Supplementary Materials for

Networks with controlled chirality via self-assembly of chiral triblock terpolymers

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Supplementary Text
Figs. S1 to S21
Fig. S1. TEM micrographs and simulated projection images. TEM micrographs with viewing along [100] (A,D,G), viewing along [110] (B,E,H) and viewing along [211] (C,F,I) of the self-assembled PI-b-PS-b-PLLA, PI-b-PS-b-PDLA and PI-b-PS-b-PLA, respectively. Insets show the corresponding simulated TEM projections.
Fig. S2. Comparison of the 1D SAXS profiles of (A) PI-b-PS-b-PLLA, (B) PI-b-PS-b-PDLA and (C) PI-b-PS-b-PLA.
Fig. S3. ECD and corresponding UV-Vis absorption spectra of polylactide-based triblock terpolymers. ECD and corresponding UV-Vis absorption spectra of polylactide-based triblock terpolymers in (A) AcCN solution and (C) the solid film. The concentration of solution is 0.1 wt%. VCD and corresponding FT-IR absorption spectra of polylactide-based triblock terpolymers in (B) CH$_2$Cl$_2$ solution and (D) the solid film. The concentration of the solution is 2 wt%.
Fig. S4. Imaging of Ni network fabricated from templating of the polylactide gyroid in the alternating gyroid of self-assembled polylactide-based triblock terpolymers. Here, the Ni network takes on the handedness and volume fraction of the particular polylactide block that is hydrolyzed. FESEM micrographs of the Ni gyroid fabricated by hydrolyzing (A) PI-\(b\)-PS-\(b\)-PLLA, (B) PI-\(b\)-PS-\(b\)-PDLA, and (C) PI-\(b\)-PS-\(b\)-PLA to make templates for electroless plating of Ni.
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Fig. S6. Polar histograms of the torsion angles in the PI-b-PS-b-PDLA sample taken from within a monograin. The chirality of the PI SG network in the PI-b-PS-b-PDLA is determined to be negative chirality for (A to I) while the region for data in (J) is distorted and inconsistent with a preferred chirality.
Fig. S7. Polar histograms of the torsion angles in the PI-b-PS-b-PLLA sample taken from within a monograin. The chirality of the PI SG network in the PI-b-PS-b-PLLA is determined to be positive for regions (A to F). Regions (G) and (H) suggest a reversed negative chirality of the network. The local torsion angles in regions (I) and (J) are mixed such that the network has a mixed character.
Fig. S8. Schematic illustration of dihedral angle and skew angle. Illustration of (A) the dihedral angle in $f_3$ and (B) the skew angle in $f_4$ of the modified Keating energy. The ideal dihedral angles of SG skeleton are 70.5° or 109.5° and ideal skew angle is 90°.
Characterization of polylactide-based triblock terpolymers synthesized.

Triblock terpolymers were synthesized by controlled living ring opening polymerization of L-lactide, D,L-lactide and D-lactide using the hydroxyl-capped diblock copolymer sample [PI-b-PS-OH (Mn = 18,200 g/mole, ĐM = 1.02)] as a macroinitiator. The successful syntheses of the triblock copolymer samples, including PI-b-PS-b-PLLA, PI-b-PS-b-PDLA, and PI-b-PS-b-PLA, via chain extension of PI-b-PS-OH with lactides can be demonstrated in comparison with the respective GPC curves (Figs. S9-11). Figs. S12-15 display the ¹H NMR spectra of the PI-b-PS-OH (Mn = 18,200 g/mole, ĐM = 1.02), PI-b-PS-b-PLLA (Mn = 41,300 g/mole, ĐM = 1.03), PI-b-PS-b-PDLA (Mn = 44,600 g/mole, ĐM = 1.05), and PI-b-PS-b-PLA (Mn = 42,900 g/mole, ĐM = 1.05), respectively. ¹H NMR spectrum of PI-b-PS-OH assignments are as follows: δ7.08 (PS, Ar-H, 3H), 6.56 (PS, Ar-H, 2H), 5.11 (PI, C=C-H, 1H), 4.72 (PI, 3,4 PI, 2H), and ¹H NMR spectrum of PI-b-PS-b-PLA assignments are as follows: δ7.08 (PS, Ar-H, 3H), 6.56 (PS, Ar-H, 2H), 5.14 (PI, C=C-H, 1H; PLA, C-H, 1H), 4.72 (PI, 3,4 PI, 2H). Accordingly, the relative volume fractions of PS, PI and polylactide blocks of the triblock terpolymer samples synthesized were determined by comparing the relative intensity of the respective ¹H resonances. The structural data determined are summarized in Table 1. Notably, the volume fractions of samples are quite asymmetric. Specifically, the volume fraction of the polylactide component is approximately 0.5 that is around 3 times of the PI component. Recently, Matsushita and co-workers also found alternating gyroid (G₃) and alternating diamond (D₄) phases in the blends of linear polyisoprene-block-polystyrene-block-poly(2-vinylpyridine) (PI-b-PS-b-P2VP) triblock terpolymers with highly asymmetric composition(28).
Scheme S1. Synthetic routes of PI-\textit{b}-PS-\textit{b}-PLLA triblock terpolymer.
Fig. S9. Comparison of GPC curves (for sample of Table 1 entry 1) between (A) PI-\textit{b}-PS-OH and (B) PI-\textit{b}-PS-\textit{b}-PLLA.
Fig. S10. Comparison of GPC curves (for sample of Table 1 entry 2) between (A) PI-\textit{b}-PS-OH and (B) PI-\textit{b}-PS-\textit{b}-PDLA.
Fig. S11. Comparison of GPC curves (for sample of Table 1 entry 3) between (A) PI-b-PS-OH and (B) PS-b-PS-b-PLA.
Fig. S12. $^1$H NMR spectra (500 MHz) of PI-$b$-PS-OH (Mn = 18,200 g/mole, ĐM = 1.02) in CDCl$_3$ (temperature = 40°C).
Fig. S13. 1H NMR spectra (500 MHz) of PI-b-PS-b-PLLA (for sample of Table 1 entry 1; Mn = 41,300 g/mole, ĐM = 1.03) in CDCl$_3$ (temperature = 40°C).
Fig. S14. 1H NMR spectra (500 MHz) of PI-b-PS-b-PDLA (for sample of Table 1 entry 2; Mn = 44,600 g/mole, DM = 1.05) in CDCl$_3$ (temperature = 40°C).
Fig. S15. 1H NMR spectra (500 MHz) PI-b-PS-b-PLA (for sample of Table 1 entry 3 Mn = 42,900 g/mole, ĐM = 1.05) in CDCl₃ (temperature = 40°C).
Thermal properties

To examine the thermal properties of the polylactide-based triblock terpolymers, the bulk samples were examined by thermogravimetry (TGA) and DSC. TGA thermograms with a plot of weight loss against temperature were carried out for PI-b-PS-b-PDLA, PI-b-PS-b-PLLA and PI-b-PS-b-PLA. As shown in Fig. S16, two degradation steps can be identified at which the first weight loss of 52 wt% starts approximately at 200°C, resulting from the weight loss of polylactide block. The thermogram appears a significant second drop, indicating that the degradation of PI and PS are overlapped with each other approximately at 340°C. Eventually, the samples will be completely degenerated. As a result, the volume fraction of polylactides block is estimated to be 0.45, in line with the NMR results.

The DSC measurements of the polylactide-based triblock terpolymers show the Tgs of PS block in PI-b-PS-b-PLLA and PI-b-PS-b-PDLA is approximately 90°C, and the Tg of polylactides in PI-b-PS-b-PLLA and PI-b-PS-b-PDLA are approximately 35°C and 38°C, respectively (Figs. S17B and C). No significant exothermic peak from crystallization can be found due to the confinement effect of vitrified PS on crystallization. Consistently, the DSC thermogram of PI-b-PS-b-PLA shows two Tg at 40°C for PLA block and 92°C for PS block (Fig. S17A). The Tgs of PI in PI-b-PS-b-PLLA, PI-b-PS-b-PDLA and PI-b-PS-b-PLA are approximately at -63°C (Fig. S18). The Tgs values of the PI in the triblock terpolymers are equivalent to the Tg of PI homopolymer (at approximately -65°C), indicating that there is no induced solubility between PI and PS segments for the terpolymers synthesized.
Fig. S16. TGA thermograms of (A) PI-PS-b-PLLA, (B) PI-PS-b-PDLA and (C) PI-PS-b-PLA. The heating rate is 10°C/min.
Fig. S17. DSC heating thermograms of (A) PI-\(b\)-PS-\(b\)-PLA, (B) PI-\(b\)-PS-\(b\)-PDLA and (C) PI-\(b\)-PS-\(b\)-PLLA samples rapidly cooled from isotropic melt. The heating rate is 10°C/min.
Fig. S18. DSC heating thermograms of (A) PI-b-PS-b-PLA, (B) PI-b-PS-b-PDLA and (C) PI-b-PS-b-PLLA samples rapidly cooled from isotropic melt. The heating rate is 10°C/min.
Identification of \( G^A \) and \( D^A \) from scattering results

To reveal the origins of different SAXS results upon samples with \( G^A \) and \( D^A \), the structure factor \( (F(q)) \) related to lattice structure in the scattering intensity \( I(q) \) is given by

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

\[
F(q) = \sum_j f_j \exp(iq \cdot r_j) \quad (2)
\]

where \( r_j \) is the position vector of \( j \)th scattering element and \( f_j \) is its form factor. The electron density \( (\rho_j) \) was assumed to be uniform in each microdomain; therefore, the form factor \( (f_j) \) is given by

\[
f_j = \rho_j f'_j \quad (3)
\]

where \( f'_j \) is the form factor free from the electron density value. By applying Equation (2) to the ordered structures of the polylactides-based triblock terpolymers and using Equation (3), we have

\[
F(q) = \sum_i f_i \exp(iq \cdot r_{ji}) + \sum_j f_s \exp(iq \cdot r_{js}) + \sum_j f_L \exp(iq \cdot r_{jL})
\]

\[
= \rho_i f'_I \sum_j \exp(iq \cdot r_{ji}) + \rho_s f'_S \sum_j \exp(iq \cdot r_{js}) + \rho_L f'_L \sum_j \exp(iq \cdot r_{jL}) \quad (4)
\]

where the subscripts \( I, S, \) and \( L \) refer to PI, PS and polylactide microdomains, respectively. Furthermore, by rewriting Equation (4) with respect to the difference of electron densities between \( I \) or \( L \) domains and the \( S \) matrix domain, the resultant equation can be derived as

\[
F(q) = \Delta \rho_I f'_I \sum_j \exp(iq \cdot r_{ji}) + \Delta \rho_L f'_L \sum_j \exp(iq \cdot r_{jL})
\]

\[\quad + \rho_s [f'_I \sum_j \exp(iq \cdot r_{ji}) + f'_S \sum_j \exp(iq \cdot r_{js}) + f'_L \sum_j \exp(iq \cdot r_{jL})] \quad (5)\]

where \( \Delta \rho_I = \rho_I - \rho_s \) and \( \Delta \rho_L = \rho_L - \rho_s \). The third term is zero in analyzing diffraction results since it denotes the scattering from the uniform electron density of \( \rho_s \). Moreover, with Miller index, the structure factor of microdomain structures can be described as

\[
F(hkl) = \Delta \rho_I f'_I \sum_j i2\pi i(x_j h + y_j k + z_j l) + \Delta \rho_L f'_L \sum_j i2\pi i(x_j h + y_j k + z_j l) \quad (6)
\]

where \((x_j, y_j, z_j)\) are the coordinates of the \( j \)th scattering element. As a result, we assumed that \( f'_I \) and \( f'_L \) are proportional to the volume fractions of PI and PLLA. Notably, the electron density of PI, PS and polylactide are 0.312 e/Å\(^3\), 0.332 e/Å\(^3\) and 0.383 e/Å\(^3\), respectively. Thus, the scattering intensity \( I(q) \) is given by

\[
I(q) = \Delta \rho_I^2 f'_I^2 \left( \sum_j i2\pi i(x_j h + y_j k + z_j l) \right)^2
\]

\[\quad + \Delta \rho_L^2 f'_L^2 \left( \sum_j i2\pi i(x_j h + y_j k + z_j l) \right)^2 \quad (7)\]
\[ I(q) \propto 9.0 \times 10^{-6} \left( \sum_j i2\pi i(x_jh + y_jk + z_jl) \right)^2 \]
\[ + 6.5 \times 10^{-4} \left( \sum_j i2\pi i(x_jh + y_jk + z_jl) \right)^2. \] (8)

It is noted that \( \Delta \rho_L^2 f'_L^2 \gg \Delta \rho_i^2 f'_i^2 \) because \( \Delta \rho_i = -0.020 \text{ e/Å}^3, \Delta \rho_L = 0.051 \text{ e/Å}^3, f'_i = 0.15V, \text{ and } f'_L = 0.5V, \) where \( V \) is the total volume. Therefore, the second term is dominant. As a result, the scattering intensity can be described as the difference between the electron densities of polylactide and PS microdomains. Accordingly, the self-assembled phases of chiral polylactide-based triblock terpolymers (PI-b-PS-b-PLLA and PI-b-PS-b-PDLA) can be recognized as an G\textsuperscript{A} structure (space group no.214, \textit{I}4\textit{1}32) instead of a double gyroid (space group no.230 \textit{I}a\textit{3}d) from X-ray scattering while the scattering contrast of PI from PS is insignificant as compared to the scattering from polylactide. Similarly, for the self-assembled phase in achiral PI-b-PS-b-PLA, the SAXS profile can be described as an D\textsuperscript{A} structure (space group no.227, \textit{Fd}3\textit{m}) instead of a double diamond (space group no.224, \textit{Pn}3\textit{m}).

Note that the \{110\} reflection in the low \( q \) region of the SAXS profile is the 4\textsuperscript{th} strongest reflection. There are arguments about the possibility to have this low \( q \) reflection, resulting from the distortion of the self-assembled structures due to dynamic deformation from sample preparation which gives “forbidden reflections” that should not appear in scattering profile from the original structure (39, 40). Notably, all the samples were annealed at 140°C for one week or even one month before characterization; there should be no concern about dynamically formed deformation. The appearance of “forbidden reflections” (e.g. the \{110\}) is attributed to the deformation of the cubic unit cell into a triclinic unit cell; yet, real-space observations confirm the presence of two interpenetrating double gyroid networks. Our 3D reconstructions clearly show single networks of both PI and polylactide in real space as shown in Figs. S19 and S20, demonstrating the G\textsuperscript{A} structure with space group \textit{I}4\textit{1}32 instead of core-shell double gyroid with space group \textit{I}a\textit{3}d.
Fig. S19. 3D visualization of single PI networks. 3D visualization of single PI gyroid network with three-fold junctions from (A) PI-\textit{b}-PS-\textit{b}-PLLA and (B) PI-\textit{b}-PS-\textit{b}-PDLA. 3D visualization of PI diamond tetrapod network from (C) PI-\textit{b}-PS-\textit{b}-PLA.
Fig. S20. Local 3D tomography and simulated results for SG and SD. (A) Local configurations of three-fold and four-fold connectors in the gyroid and the diamond structures, respectively. The gyroid lattice is a chiral structure constructed with inter-node dihedral angle of $+70.5^\circ$ and $+250.5^\circ$ (positive chirality for clockwise rotation (+)) or $-70.5^\circ$ and $-250.5^\circ$ (negative chirality for counterclockwise rotation (-)) whereas the diamond lattice is an achiral structure. (B) The reconstructed images of three-fold and four-fold connecting node from 3D TEM.
Chirality (torsion angle analysis)

For systematic examination of the chirality of self-assembled G² from the polylactide-based chiral triblock terpolymers, electron tomography is one of reliable approaches. With the proposed method of torsion angle analysis, it is feasible to examine the controlled chirality from the simplest building unit (dihedral of the trigonal planar). As a result, tomographic experiments were carried out on OsO₄-stained samples to directly visualize the PI single gyroid from the triblock terpolymers. However, the RuO₄-stained samples with dark PS matrix is not able to distinguish the polylactide single gyroid and the PI single gyroid in the reconstruction. This is caused by the difficulty to reconstruct the bright network from dark matrix. The polylactide single gyroid is not able to be stained to give required mass-thickness contrast for reconstruction from the PS matrix; for the one with replacement of the network texture by templated electroless plating of nickel, it is also impractical for the aimed reconstruction due to the strong scattering encountered from the nickel. For the chirality analysis, to be representative, reliable and meaningful from the reconstruction, we did carry out the reconstruction by selecting large enough monograins from different locations and various samples for representative results. Considering the statistical analysis, we selected ten representative reconstruction images with reliable resolution for the torsion angle analysis through the proposed thinning approach to produce the skeletal network with more than at least 100 datasets for the determination of torsion angle from one reconstruction result (monograin); in total, there are more than 1000 datasets for the determination of torsion angle in each sample synthesized.
Anisotropic effect on ECD spectrum

There is no significant variation on the linear dichroism (LD) signals from 200 to 300 nm for chiral polylactide-based triblock terpolymers (Fig. S21), indicating that there should be no observable anisotropic effect on spectroscopic measurements in the solution. Those results assure that the ECD signals are mainly contributed by the chiral entity in the constituted chiral blocks of the triblock terpolymers.

Fig. S21. LD spectra of polylactide-based triblock terpolymers. LD spectra of polylactide-based triblock terpolymers in (A) AcCN solution and (B) the solid film. The concentration of solution is 0.1 wt%.