Supporting Information

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The Supporting Information contains the following information and figures.

1. Description of the methods of analysis of the polymers synthesized in this study.
2. $^1$H (400 MHz) NMR spectrum of sPP-$b$-PS (Figure S1)
3. GPC curves of the polymers synthesized (Figure S2)
4. Theoretical SAXS curves of OBDD and OBDG phase (Figure S3).
5. Entire temperature-dependent SAXS profiles of sPP-$b$-PS (Figure S4 and S5).
6. DSC heating scan of sPP-$b$-PS (Figure S6)
7. SAXS profile of sPP-$b$-PS collected at room temperature after the sample has been isothermally annealed at 140 °C for 24 h (Figure S7)
8. A TEM micrograph of sPP-$b$-PS (Figure S8).
9. Entire temperature-dependent FTIR spectra of sPP-$b$-PS (Figure S9).
10. SAXS profiles of neat sPP-$b$-PS and sPP-$b$-PS/sPP blends (Figure S10).
**Analysis of the Polymers Synthesized in this Study.**

The molecular weight and molecular weight distribution (MWD) of the polymers synthesized in this study were determined by gel permeation chromatography (Waters 150-CALAC/GPC) with a refractive index (RI) detector and a set of U-Styragel HT columns of $10^6$, $10^5$, $10^4$ and $10^3$ Å pore sizes in series. The measurements were taken at 135 °C using 1, 2, 4-trichlorobenzene as solvent. PS samples with narrow MWDs were used as the standards for calibration. The standards were in the range of absolute molecular weight, which is from 980 to 2110000, and the $R$ square of the ideal calibrated line was limited to up to 0.999.

All $^1$H NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer. The sPP-$b$-aPS sample was dissolved in CDCl$_3$ as solvent, and the recording temperature was 60 °C.
Figure S1. $^1$H (400 MHz) NMR spectrum of sPP-$b$-PS ($M_n = 16200$ g/mol, PDI = 1.19). (Solvent CDCl$_3$; temperature: 60 °C)
Figure S2. GPC curve of (a) pMS-capped sPP ($M_n = 6800$ g/mole, $M_w/M_n = 1.32$), (b) polystyrene (PS, $M_n = 9400$ g/mole, $M_w/M_n = 1.02$) and (c) sPP-$b$-aPS ($M_n = 16200$ g/mole, $M_w/M_n = 1.19$) (solvent 1, 2, 4-trichlorobenzene; temperature 135 °C).
Figure S3. The theoretical scattering profiles of OBDD and OBDG phase calculated by assuming $Pn\bar{3}m$ and $Ia\bar{3}d$ space group symmetry, respectively, with the 3D network structure constructed by cylindrical microdomains. The algorithm and model adopted were developed by Förster et al., which took into account the domain size distribution, distortion of domain spacing, grain size and peak shape which varied analytically between Lorentzian and Gaussian functions. It can be seen that the OBDD structure exhibits five diffraction peaks with position ratio of $1: (3/2)^{1/2}: 2^{1/2}: 3^{1/2}: 4^{1/2}$, corresponding to (110), (111), (200), (211) and (220) planes, respectively. The OBDG structure displays four diffraction peaks with position ratio of $1: (4/3)^{1/2}: (7/3)^{1/2}: (11/3)^{1/2}$, corresponding to (211), (220), (321) and (332) planes, respectively.
**Figure S4.** Temperature-dependent SAXS profiles of as-cast sPP-b-PS obtained in a heating cycle, where each profile was collected after annealing at each temperature for 5 min and followed by data acquisition for 5 min. The red curves represent the calculated SAXS curves of OBDD and OBDG structures.
Figure S5. Temperature-dependent SAXS profiles of as-cast sPP-b-PS, where each profile was collected after annealing at each temperature for 30 min and followed by data acquisition for 1 h.
Figure S6. DSC heating scan (heating rate = 5 °C/min) of sPP-b-PS. The melting point ($T_m^{\text{sPP}}$) and the end of melting ($T_{mh}^{\text{sPP}}$) of sPP crystallites are 124 °C and 137 °C, respectively.
**Figure S7.** The SAXS profile of sPP-\(b\)-PS collected at room temperature after the sample has been isothermally annealed at 140 °C for 24 h and then quenched to liquid nitrogen. The red curve represents the calculated SAXS curve of OBDD structure.
Figure S8. (a) The transmission electron microscopy (TEM) micrograph obtained of an ultrathin section of sPP-b-PS film. The ultrathin section was stained with the vapor of 0.5 wt% RuO₄(aq) for 20 min. The PS phase appears as the dark region in the micrograph while sPP phase corresponds to the bright region. (b) Characteristic view of a double-diamond lattice model from [100] direction. This picture was reproduced from ref. 17.
Figure S9. Temperature-dependent FTIR spectra of as-cast sPP-b-PS, in which “HI” and “HA” mean that the signals of helical chain conformation of sPP blocks in the crystalline state (at 1005, 903, 867 and 812 cm\(^{-1}\)) and those in the non-crystalline state (at 977, 844 and 836 cm\(^{-1}\)), respectively. The spectrum of PS homopolymer is shown in the bottom.
Figure S10. The SAXS profiles of neat sPP-b-PS ($f^\text{sPP} = 0.46$) and sPP-b-PS/sPP homopolymer blends ($f^\text{sPP} = 0.48$ and 0.52).