Electronic Supplementary Information

Spiral- and Meridian-Patterned Spheres Self-Assembled from Block Copolymer/Homopolymer Binary Systems

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Polymer Syntheses and Characterizations

1. Materials and regents

α-Methoxy-ω-amino poly(ethylene glycol) (mPEG-NH_2, M_n = 5 kg·mol^{-1}) was purchased from Sigma-Aldrich. γ-Benzyl-L-glutamate-N-carboxyanhydride (BLG-NCA) was synthesized according to literatures.[S1-S3] Styrene (St) was distilled before use. CuBr was purified by stirring in acetone overnight, filtered and washed with acetone for three times then dried under vacuum at room temperature. Ethyl 2-bromoisobutyrate (EtBriB) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) were used as received. 1,4-Dioxane was dried by reflux before use. Other materials were obtained from Adamas-beta, and purified according to conventional methods or used as received. Deionized water was prepared in a Millipore Super-Q Plus Water System to a level of 18.2 MΩ·cm resistance. Dialysis bag (Membra-cel, 3500 molecular weight cutoff) was provided by Serva Electrophoresis GmbH.

2. Synthesis and characterization of PBLG-*b*-PEG and PBDG-*b*-PEG block copolymers

Poly(γ-benzyl-L-glutamate)-*block*-poly(ethylene glycol) (PBLG-*b*-PEG) BCPs were synthesized by ring-opening polymerization of BLG-NCA in anhydrous 1,4-dioxane initiated by mPEG-NH_2 according to our previous work.[S4,S5] The reaction was performed in flame-dried reaction bottle under a dry nitrogen atmosphere for 3 days at 15 ºC. The resulting products were purified twice by repeated precipitation from a chloroform solution into a large volume of anhydrous methanol. PBDG-*b*-PEG BCPs were synthesized with the similar process by using γ-Benzyl-D-glutamate-N-carboxyanhydride (BDG-NCA) as starting monomer.

The molecular weight of PBLG-*b*-PEG and PBDG-*b*-PEG BCPs were estimated using nuclear magnetic resonance (^{1}H NMR) measurement (Avance 550, Bruker) in the solvent of chloroform-d ($CDCl_3$) and trifluoroacetic acid-d (TFA-d) mixture. Since the molecular weight of the PEG block is known (M_n = 5 kg·mol^{-1}), the number-average molecular weight (M_n) and the degree of polymerization (DP) of PBLG blocks can be calculated from the intensity ratio of the methylene proton signal (5.1 ppm) of polypeptide to the ethylene proton signal (3.6 ppm) of PEG. The Đ of them were obtained from gel permeation chromatography (GPC) testing (PL 50 plus, DMF (20 mmol/L LiBr) as eluent solvent).

3. Synthesis and characterization of PS homopolymers

Polystyrene (PS) homopolymers were synthesized by atom transfer radical polymerization (ATRP) with EtBriB as initiator.[S6,S7] EtBriB, St, CuBr, and PMDETA were added into a Schlenk flask. The mixture was purged with dry nitrogen and subjected to three freeze-pump-thaw cycles to remove any dissolved oxygen. The Schlenk flask was then sealed with nitrogen and immersed in a thermostatic oil bath at 70 ºC. After 24 h, the mixture was diluted with tetrahydrofuran and stirred under air to stop the reaction. Then copper salts in the mixture were removed through a plugged column of neutral aluminum oxide. After concentrating the solvent by reduced pressure distillation, the PS homopolymers were precipitated in a large volume of cold methanol. Finally, the white powder was obtained by drying in a vacuum oven.

The ^{1}H NMR spectra shows the structure information of PS homopolymer. 6.5-7.1 ppm are the proton peaks of aromatic groups, 1.0-2.8 ppm are the peaks of backbone protons. The molecular weight and Đ of PS homopolymer were obtained by GPC testing.

Characterization Methods

1. Ultraviolet-Visible Spectrophotometer (UV-Vis)

Turbidity data were measured by UV-Vis spectrophotometer with the wavelength of 690 nm. A THF/DMF (7/3, v/v) mixture solvent was used as the reference. The polymer solution (c = 0.2 g/L, V = 2 mL, solvent: THF/DMF = 7/3, v/v) was placed in a cuvette. Under magnetic stirring, water was added drop by drop. After each of the water dropping, the absorbance of polymer solution at 690 nm was recorded and compared with that of the reference solvent.

2. Scanning Electron Microscopy (SEM)

The surface profile of the aggregates was obtained from Field Emission SEM (S4800, Hitachi) operated at an accelerating voltage of 15 kV. The sample was prepared by placing drops of solution on a Si Wafer and then was dried at room temperature. Before observation, the samples were sputtered by platinum.

3. Wide-Angle X-ray Scattering (WAXS)

The sample solution was freeze-drying under vacuum to obtain a powder sample for the WAXS testing. Synchrotron radiation WAXS measurement was performed at beamline BL16B1 of Shanghai Synchrotron Radiation Facility. The wavelength of X-ray is 0.124 nm (E = 10 keV), and the distance of sample to detector for WAXS is calibrated to be 207.51 mm. The exposure time was 60 s. Two-dimensional WAXS pattern is collected with a Mar165 CCD detector (2048 × 2048 pixels with a pixel size of 80 μm). The WAXS data is analyzed with Fit2D software from the European Synchrotron Radiation Facility. The d-spacing values are calculated from Bragg's Law $d = 2\pi/q$.[S8-S10]

Supplementary Table and Figures

Table S1. Characterization of polymers

Sample	M_n[a] (kg•mol^{-1})		DP[a]		Đ[b]
PBLG$_{41}$-*b*-PEG$_{112}$	PBLG: 8.9k	PEG: 5k	PBLG: 41	PEG:112	1.18
PBLG$_{75}$-*b*-PEG$_{112}$	PBLG: 16.4k	PEG: 5k	PBLG: 75	PEG:112	1.15
PBLG$_{111}$-*b*-PEG$_{112}$	PBLG: 24.3k	PEG: 5k	PBLG: 111	PEG:112	1.12
PBDG$_{83}$-*b*-PEG$_{112}$	PBDG: 18.1k	PEG: 5k	PBLG: 83	PEG:112	1.15
PS$_{38}$	PS: 4.0k		PS: 38		1.04
PS$_{62}$	PS: 6.4k		PS: 62		1.08
PS$_{245}$	PS: 25.4k		PS: 245		1.13

[a] For PBLG-*b*-PEG and PBDG-*b*-PEG BCPs, since the M_n value and DP of the PEG segment is known, the M_n and DP of PBLG and PBDG blocks were derived according to ^{1}H NMR spectra in CDCl$_3$. For PS homopolymers, their M_n values were obtained by GPC testing using DMF (20 mmol/L LiBr) as eluent solvent.

[b] The Đ values of polymers were obtained from GPC testing.

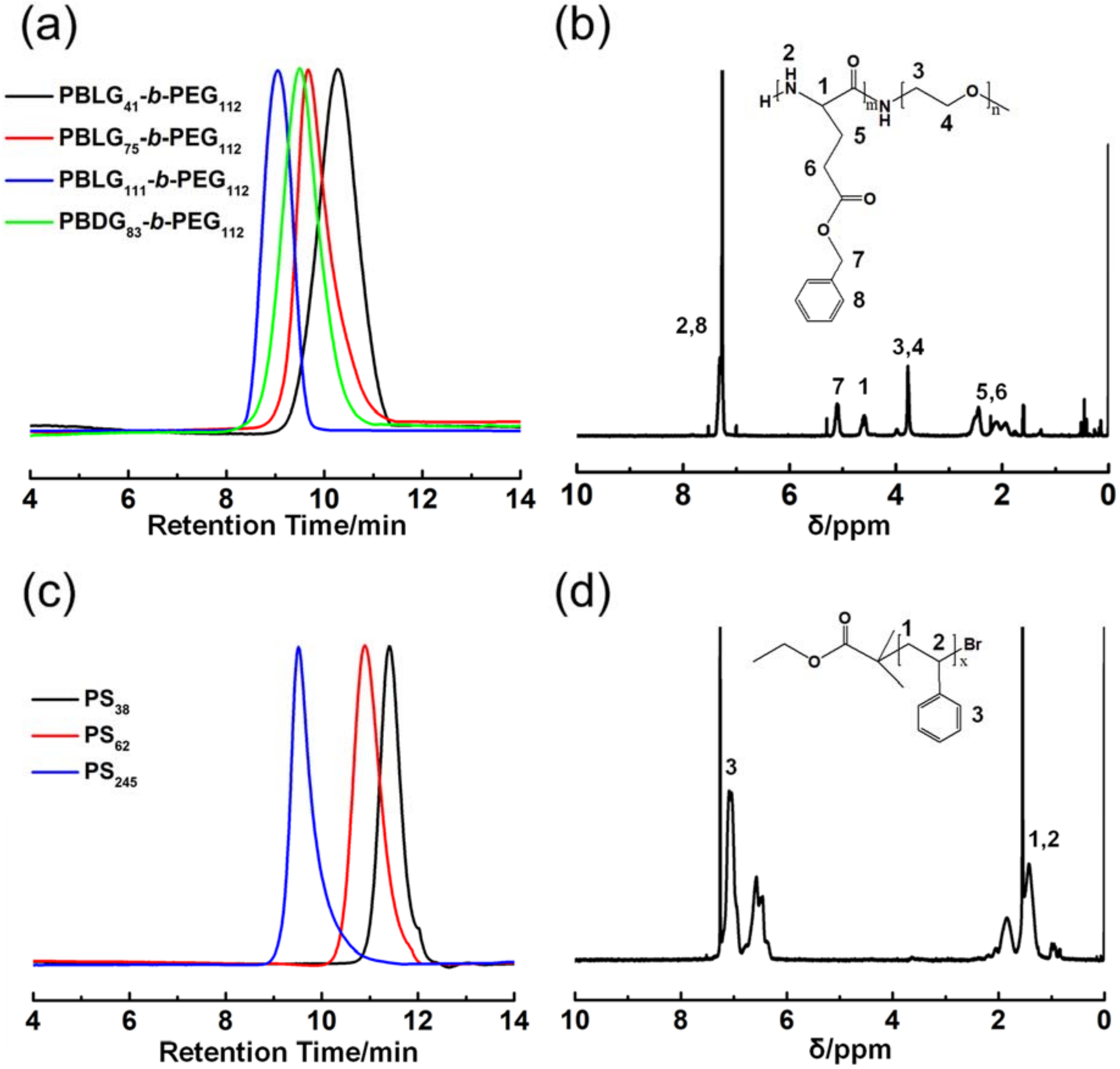

Figure S1. GPC curves and ^{1}H NMR spectra of PBLG-*b*-PEG BCPs, PBDG-*b*-PEG BCPs, and PS homopolymers, respectively.

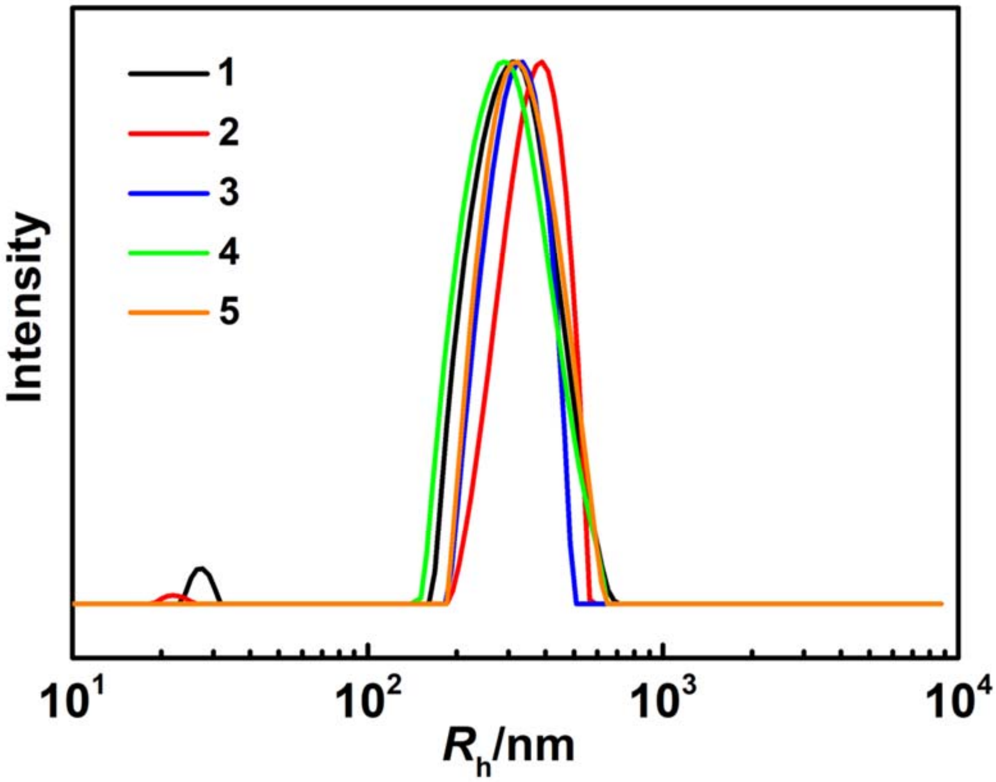

Figure S2. Dynamic light scattering (DLS) for the apparent hydrodynamic radius (R_h) distribution of the stripe-patterned spheres self-assembled from PS_{62} homopolymers and $PBLG_{75}$-*b*-PEG_{112} block copolymers at various conditions (scattering angle: 90°). Line 1: spiral spheres, T = 20 °C, f_{DMF} = 0.5, R_h = 355 nm; Line 2: spiral spheres, T = 40 °C, f_{DMF} = 0.5, R_h = 368 nm; Line 3: meridian spheres, T = 60 °C, f_{DMF} = 0.5, R_h = 357 nm; Line 4: spiral spheres, T = 20 °C, f_{DMF} = 0.3, R_h = 345 nm; Line 5: spiral spheres, T = 20 °C, f_{DMF} = 0.7, R_h = 357 nm.

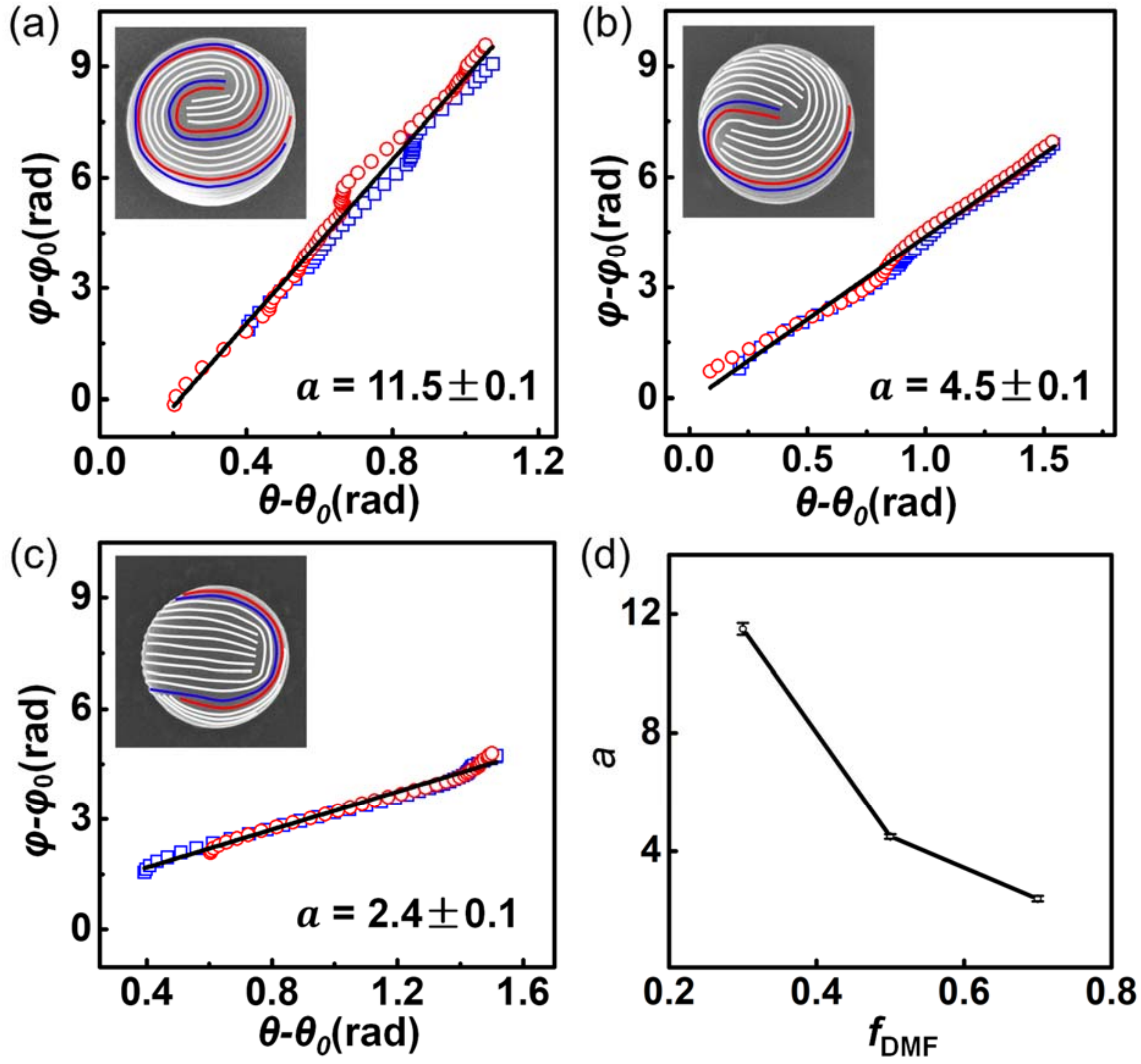

Figure S3. (a-c) The relation between φ to θ values of spirals formed with various f_{DMF}: (a) $f_{\mathrm{DMF}} = 0.3$, $\boldsymbol{a} = 11.5\pm0.1$; (b) $f_{\mathrm{DMF}} = 0.5$, $\boldsymbol{a} = 4.5\pm0.1$; (c) $f_{\mathrm{DMF}} = 0.7$, $\boldsymbol{a} = 2.4\pm0.1$. The insets in (a-c) are SEM images of spirals prepared with corresponding initial solvents at 20 $^{\circ}$C. (d) Plots of the DMF content in the initial solvent (f_{DMF}) versus the increment ratio of φ to θ ($(\varphi-\varphi_0)/(\theta-\theta_0) = \boldsymbol{a}$).

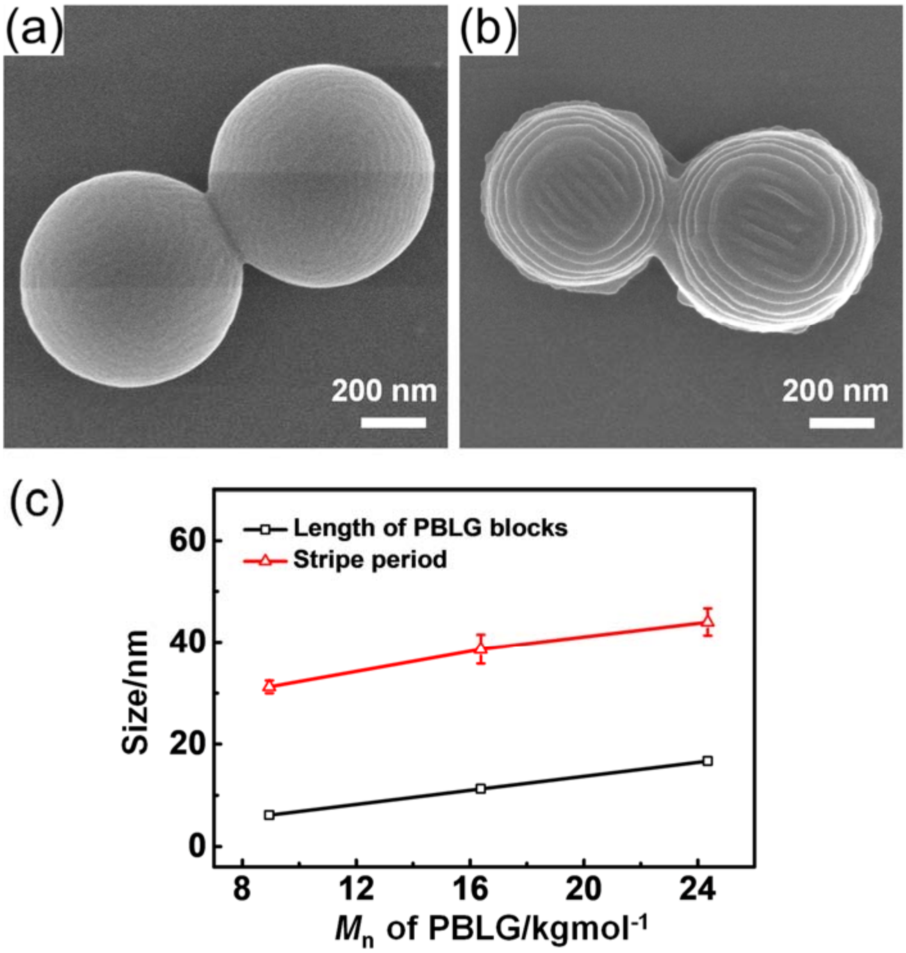

Figure S4. The effect of M_n of PBLG blocks on surface pattern. (a,b) SEM images of spiral spheres self-assembled from co-assembly of PS_{62} homopolymer with different block copolymers: (a) $PS_{62}/PBLG_{41}$-*b*-PEG_{112}; (b) $PS_{62}/PBLG_{111}$-*b*-PEG_{112}. $f_{DMF} = 0.3$, $T = 20\ ^oC$. (c) Plots of the length of the PBLG block versus the width and domain spacing of the surface stripes formed by PBLG-*b*-PEG/PS_{62} systems with various M_n of PBLG blocks. The period of stripes increases approximately linearly with the M_n of the PBLG blocks.

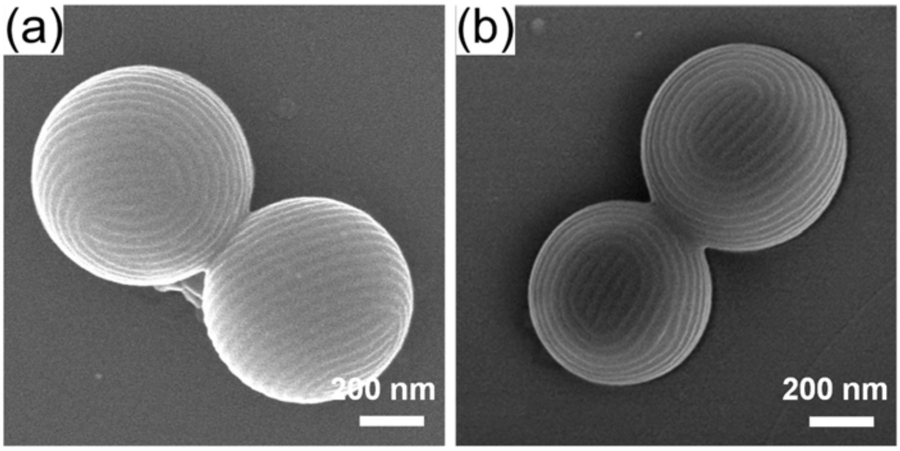

Figure S5. The effect of molecular weight of PS blocks on surface pattern. (a,b) SEM images of spiral spheres self-assembled from co-assembly of PBLG$_{75}$-*b*-PEG$_{112}$ BCPs with different PS homopolymers: (a) PS$_{38}$/PBLG$_{75}$-*b*-PEG$_{112}$; (b) PS$_{245}$/PBLG$_{75}$-*b*-PEG$_{112}$. f_{DMF} = 0.3, T = 20 °C.

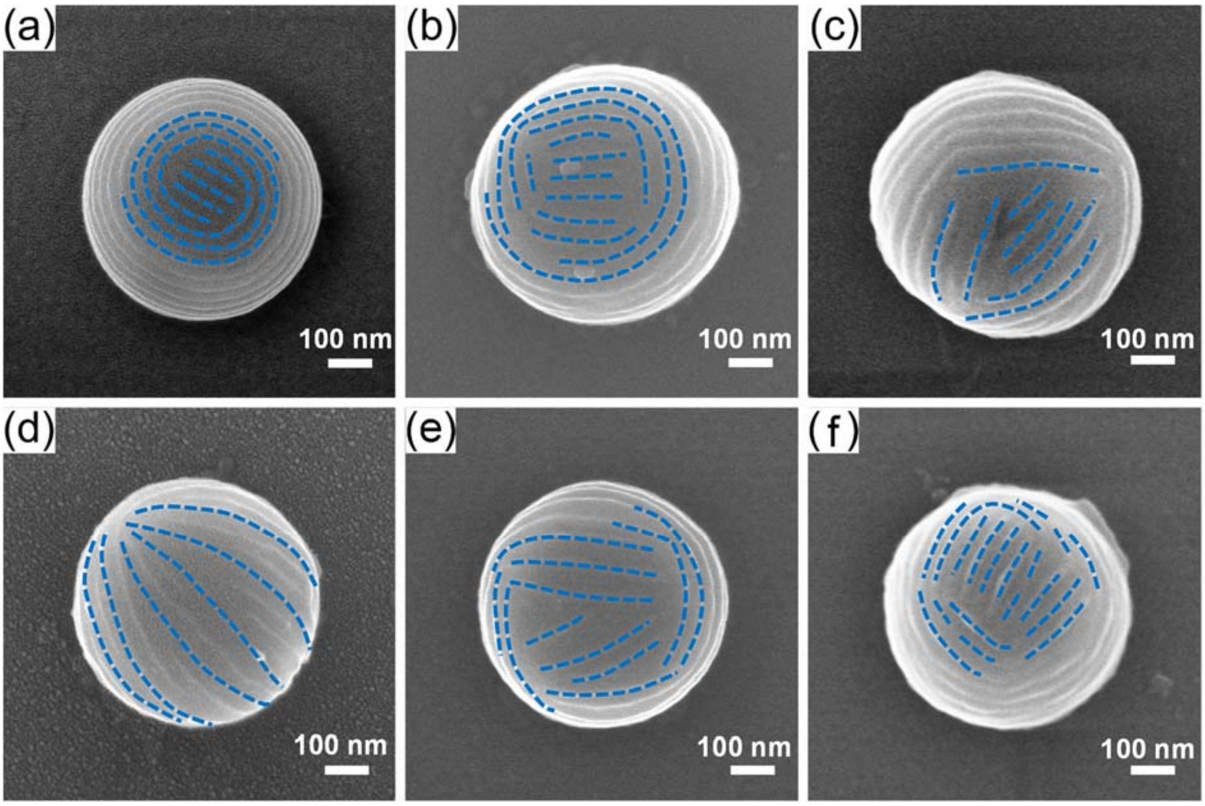

Figure S6. Effect of mixing ratio of $PBLG_{75}$-*b*-PEG_{112}/$PBDG_{83}$-*b*-PEG_{112} on the surface pattern. SEM images of striped spheres self-assembled from $PBLG_{75}$-*b*-PEG_{112}/$PBDG_{83}$-*b*-PEG_{112}/PS_{62} mixtures with various $PBLG_{75}$-*b*-PEG_{112}/$PBDG_{83}$-*b*-PEG_{112} weight ratios: (a) 0/3; (b) 0.5/2.5; (c) 1/2; (d) 1.5/1.5; (e) 2/1; and (f) 2.5/0.5. All the samples were prepared with $f_{DMF} = 0.3$ and $T = 20$ °C.

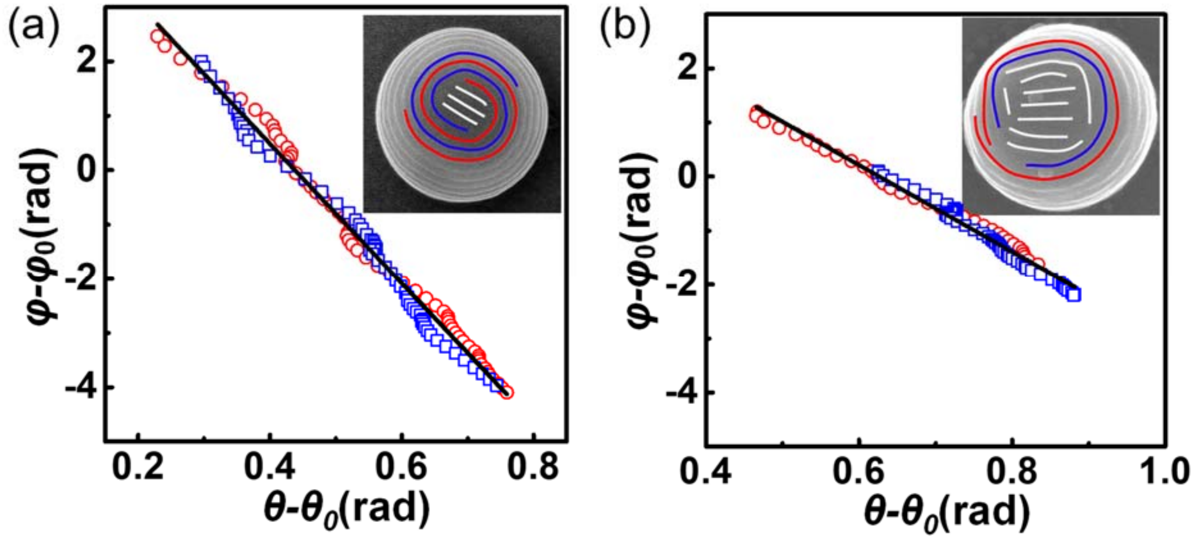

Figure S7. The relation between φ to θ values ((φ-φ_0)/(θ-θ_0) = $\boldsymbol{a}$) of spirals formed with various PBLG$_{75}$-*b*-PEG$_{112}$/PBDG$_{83}$-*b*-PEG$_{112}$ weight ratios: (a) 0/3, $\boldsymbol{a}$ = -12.8±0.1; and (b) 0.5/2.5, $\boldsymbol{a}$ = -8.0±0.1. The insets are corresponding SEM images of spirals. All the samples were prepared with f_{DMF} = 0.3 and T = 20 ^{o}C.

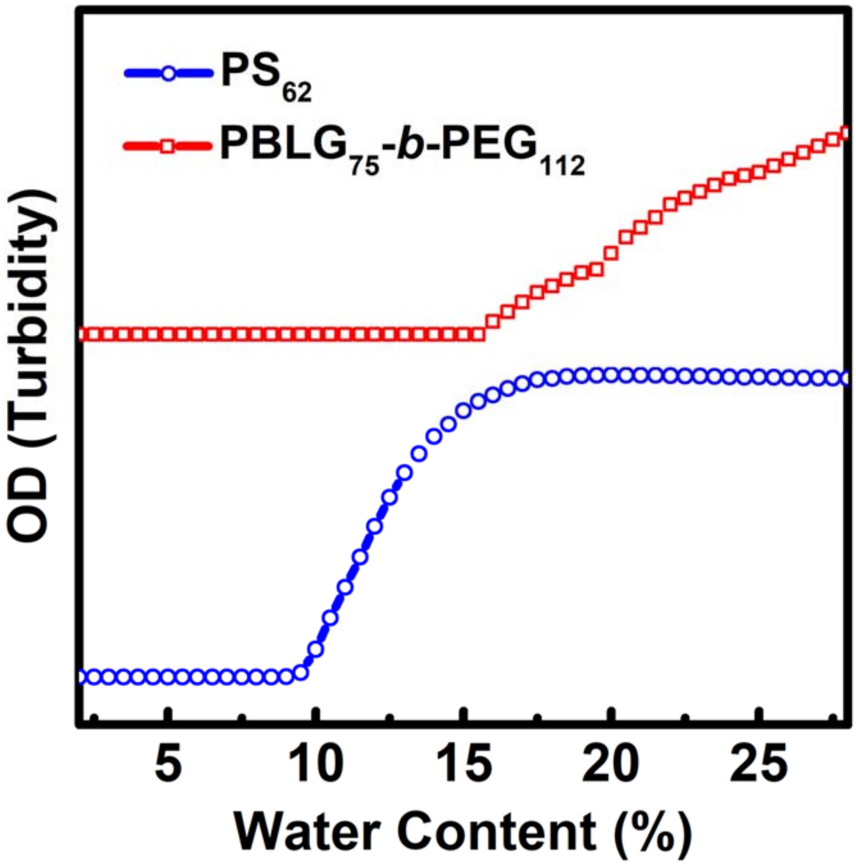

Figure S8. Turbidity (optical density) curves of PBLG$_{75}$-*b*-PEG$_{112}$ block copolymers and PS$_{62}$ homopolymers as a function of added water content to the solutions. The CWC of PS$_{62}$ and PBLG$_{75}$-b-PEG$_{112}$ were 9.3 vol% and 16.1 vol%, respectively.

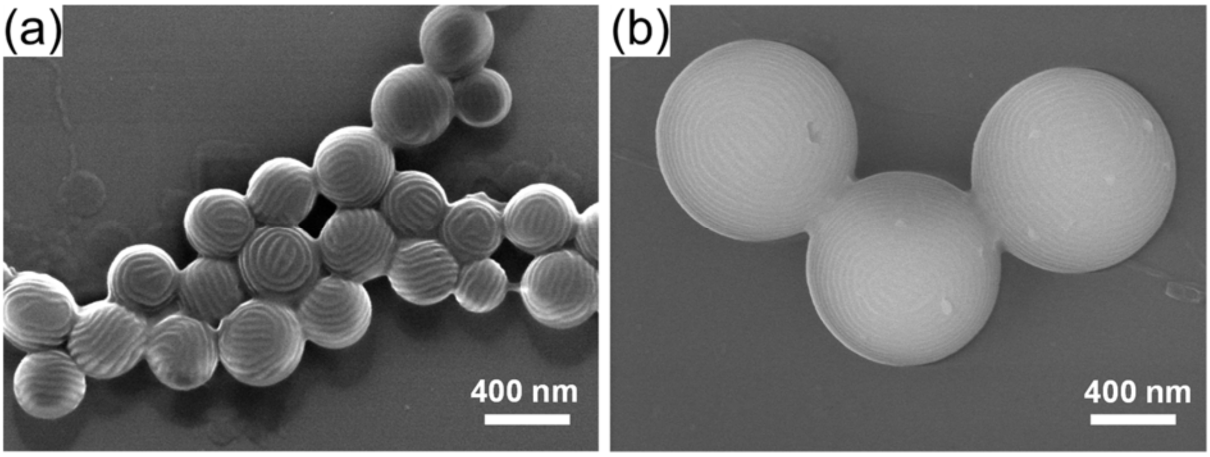

Figure S9. Spiral spheres self-assembled from $PBLG_{75}$-*b*-PEG_{112} block copolymers and PS_{62} homopolymers by a two-step method with different adding rate of water. (a) Adding rate of water is 0.34 mL/min, average diameter of the spiral spheres is 340 nm; (b) Adding rate of water is 0.017 mL/min, average diameter of the spiral spheres is 950 nm. All the samples were prepared with f_{DMF} = 0.3 and T = 20 ^{o}C.

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