

Electronic Supplementary Information

for

Self-Assembly of Dendritic-Linear Block Copolymers With Fixed Molecular Weight and Block Ratio

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Materials and Methods.

All reagents and chemicals were purchased from commercial sources and used as received. All reactions were performed under N₂ unless otherwise noted. NMR spectra were recorded on a Varian VNMRS 600 spectrometer with CDCl₃ as a solvent. Molecular weights of block copolymers were measured on a Agilent 1260 Infinity GPC system equipped with a PL gel 5 μ m mixed C column (Polymer Laboratories)) and differential refractive index detectors. THF was used as an eluent with a flow rate of 1 mL/min. A PS standard (Polymer Laboratories) was used for calibration. MALDI-TOF was performed on a Bruker Ultraflex III TOF-TOF mass spectrometer equipped with a nitrogen laser (335 nm) and operating in a reflectance mode. Internal calibration was performed using a Bruker peptide calibration standard (mass range 1000–4000 Da). The analytical sample was obtained by mixing a THF solution of analyte (5-10 mg/mL) with a THF solution of matrix (2,5-dihydroxybenzoic acid, 10 mg/mL) in a 1/5 v/v ratio. The prepared solution of the analyte and matrix (0.5 μ L) was loaded on the MALDI plate and allowed to dry at 23 °C before the plate was inserted into the vacuum chamber of the MALDI instrument. The laser steps and voltages applied were adjusted depending on both the molecular weight and the nature of analyte.

Transmission electron microscopy (TEM) was performed on a JEOL 1400 microscope at an acceleration voltage of 100 kV. Sample specimens were prepared by placing a drop of the solution on a carbon-coated Cu grid (200 mesh, EM science). After 30 min, remaining solution on a grid was removed with a filter paper, and the grid was air-dried for 8 h.

The turbidity test was performed on a JASCO V-670 UV-Vis spectrophotometer equipped with a thermostat sample holder with a magnetic stirrer. 1.5 mL of dioxane solution of a block copolymer (0.5 wt %) was stirred while water was added through a syringe pump at a rate of 1.5 mL/h. Absorbance at 480 nm was measured at every 30 second for 1 h.

Synthesis of Dendritic Macroinitiators with Peripheral PEG Chains.

Polymerization of PEG-*b*-PS. Dendrons **1–8** and macroinitiators **L1** and **D1–D3** were synthesized by following the literature procedure.^{1,2}

L1. Monomethoxy PEG (1 g, $M_n = 3000$ g/mol, Polymer Source, Montreal, Canada) and triethylamine (0.1 mg, 1 mmol) were dissolved in dry THF (50 mL). To this solution was added dropwise α -bromoisobutryl bromide (0.23 g, 1mmol) in 3 mL dry THF. The solution was stirred for 24 h at room temperature. White solid was removed by filtration. The filtered solution was evaporated on a rotavap and the resulting residue was redissolved in CH_2Cl_2 (10 mL), which was precipitated into cold diethyl ether. White solid was collected by vacuum filtration. White solid was obtained after drying in vacuo. Yield 0.9 g, ^1H NMR (δ =ppm, 600 MHz, CDCl_3) 4.33 (t, 2H), 3.76-3.52 (m, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.38 (s, 3H), 1.94 (s, 6H). M_n (GPC) = 4020 g/mol, PDI = 1.08, M_n (MALDI-TOF) = 3125 g/mol.

D1. Yield. 2.4 g, ^1H NMR (δ =ppm, 600 MHz, CDCl_3) 6.6 (s, 2H), 5.1 (s, 2H), 4.12-4.15 (m, 6H), 3.70-3.54 (m, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.38 (s, 3H), 1.95 (s, 6H). M_n (GPC) = 4020 g/mol, PDI = 1.03. M_n (MALDI-TOF) = 3255 g/mol.

D2. Yield 1.8 g, ^1H NMR (δ =ppm, 600 MHz, CDCl_3) 6.68 (s, 2H), 6.63 (s, 4H), 6.61 (s, 2H), 5.06 (s, 2H), 5.01 (s, 4H), 4.97 (s, 2H), 3.80-3.54 (m, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.35 (m, 27H), 1.91 (s, 6H). M_n (GPC) = 3410 g/mol, PDI = 1.04. M_n (MALDI-TOF) = 3702 g/mol.

D3. Yield 3.1 g, ^1H NMR (δ =ppm, 600 MHz, CDCl_3) 6.60 (s, 2H), 5.10 (s, 2H), 4.16-4.13 (m, 6H), 3.71-3.50 (m, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.38 (s, 9H), 1.95 (s, 6H). M_n (GPC) = 3350 g/mol, PDI = 1.04. M_n (MALDI-TOF) = 2736 g/mol.

Synthesis of block copolymers.

Polymerization of styrene was performed with macroinitiators under a standard ATRP condition.²

Representative procedure: CuBr (7 mg, 0.05 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (12 mg, 0.075 mmol) were mixed with 1 mL of anisole in a 20 mL Schlenk tube with a magnetic bar. The tube was sealed with a rubber septum. This mixture was bubbled with N_2 for 15 min

with gentle stirring. To this solution, the solution of styrene (5 mL) and **D1** (120 mg, 0.035 mmol) was added via a syringe. The green solution was degassed by bubbling N₂ for 20 min. After degassing, the tube was immersed in a preheated oil bath (95 °C) and the polymerization was proceed at this temperature. The progress of polymerization was monitored by taking GPC at an interval of 1 h. When the molecular weight of the block copolymer reached to the desired value, the reaction was quenched by exposing the solution to air in an ice/water bath and diluted with CHCl₃ (15 mL). The cooled solution was filtered through a pack of aluminum oxide (basic) with CHCl₃ to remove the Cu catalyst. The filtered solution was concentrated on a ratavap, and the resulting residue was diluted with 20 mL CH₂Cl₂. This solution was precipitated into methanol (400 mL). White powder was collected by vacuum filtration and dried in vacuo. All block copolymers were characterized by ¹H NMR and GPC to evaluate the molecular weight and the size distribution. The molecular characteristics of the block copolymers are listed in **Table S1**.

Preparation of Micelle Solutions. Doubly distilled water (MilliQ, 18.1 MΩ) was used throughout the experiments. A typical procedure is described: 3(PEG₂₂)-PS₁₅₂ (10 mg) was dissolved in 1,4-dioxane (dioxane) (2 mL) in a 15 mL capped vial with a magnetic stirrer. The solution was stirred for 3 h at room temperature. A syringe pump was calibrated to deliver water with a speed of 2 mL/h. The vial cap was replaced by a rubber septum. 2 mL of water was added to the organic solution with vigorous stirring (850 rpm) by a syringe pump with a 5 mL syringe equipped with a steel needle. After adding 2 mL of water, 50 μL of the suspension was taken and added at once in 2 mL of pure water with stirring. This ensured a rapid quenching of the PS domain of micelles. The remaining solution was subjected to dialysis (SpectraPor, molecular weight cut-off: 12,000–14,000 Da) against water for 24 h with a frequent change of water. After dialysis, all organic solvents were replaced with water. Dialysis performed longer than 24 h did not change morphology of micelles. In all cases, the morphology of the micelles after rapid quenching and dialysis for 24 h was identical based on the TEM observation.

Table S1. Molecular characteristics of the block copolymers

entry	M_n (GPC) ^a (kg/mol)	PDI (GPC) ^a	DP_n^{PS} (¹ H NMR) ^b	W_{PEG} (%) ^c
PEG ₆₈ -PS ₁₅₃	19.2	1.13	159	15.6
PEG ₆₈ -PS ₁₇₀	20.9	1.08	176	14.3
3(PEG ₂₂)-PS ₁₂₀	15.8	1.07	114	18.9
3(PEG ₂₂)-PS ₁₅₂	19.3	1.08	156	15.5
3(PEG ₂₂)-PS ₁₇₁	21.1	1.08	177	14.2
9(PEG ₇)-PS ₁₂₁	16.3	1.07	116	19.3
9(PEG ₇)-PS ₁₅₀	19.4	1.08	151	16.2
9(PEG ₇)-PS ₁₆₆	21.0	1.08	171	15.0

^aMolecular weights and polydispersity index measured by gel permeation chromatography (GPC). ^bCalculated number average degree of polymerization from the ¹H NMR integration (PEG vs aromatic signal of PS). ^cThe calculated weight fraction of a PEG block in the block copolymers based on GPC results.

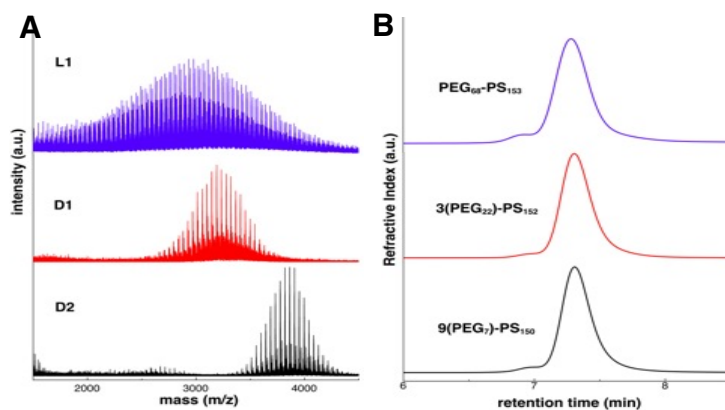


Fig. S1. (A) MALDI-TOF spectra a linear PEG (**L1**) and PEG-based macroinitiators (**D1**, **D2**). Excluding the dendritic benzyl ether scaffold, the molecular weight of the PEG segment determined by MALDI-TOF was 2998 g/mol for **D1** and 3140 g/mol for **D2**, which are close to the molecular weight of the linear PEG analog **L1** (3020 g/mol). (B) GPC traces of block copolymers containing a linear and dendritic PEG block.

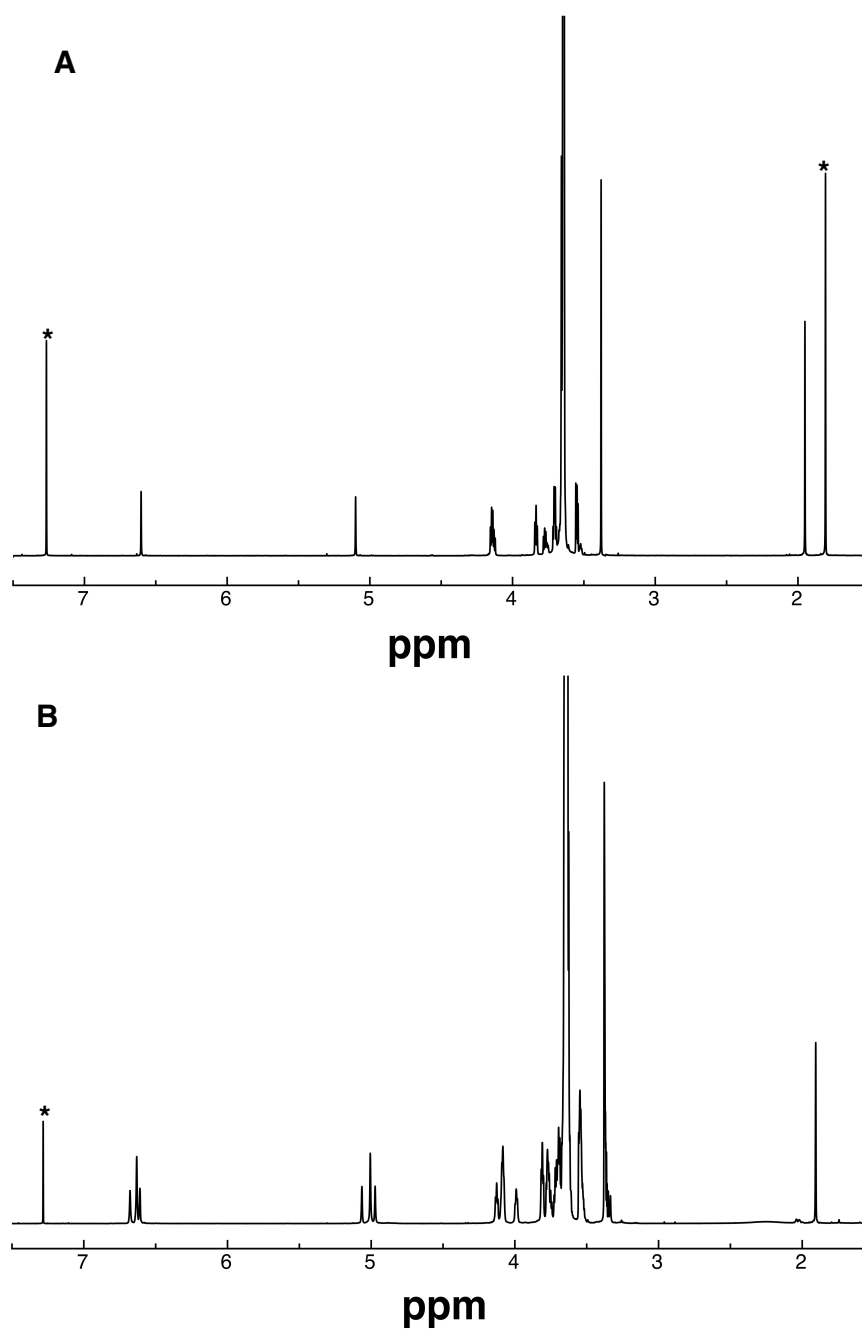


Fig. S2. ¹H NMR spectra of dendritic macroinitiators **D1** (A) and **D2** (B) in CDCl₃. * indicates residual solvents.

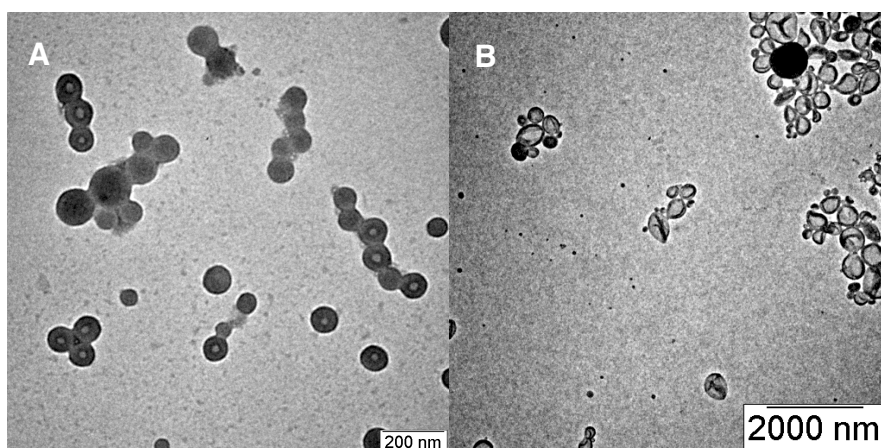


Fig. S3. TEM images of vesicles of PEG₆₈-PS₁₅₃ prepared from (A) THF and (B) dioxane.

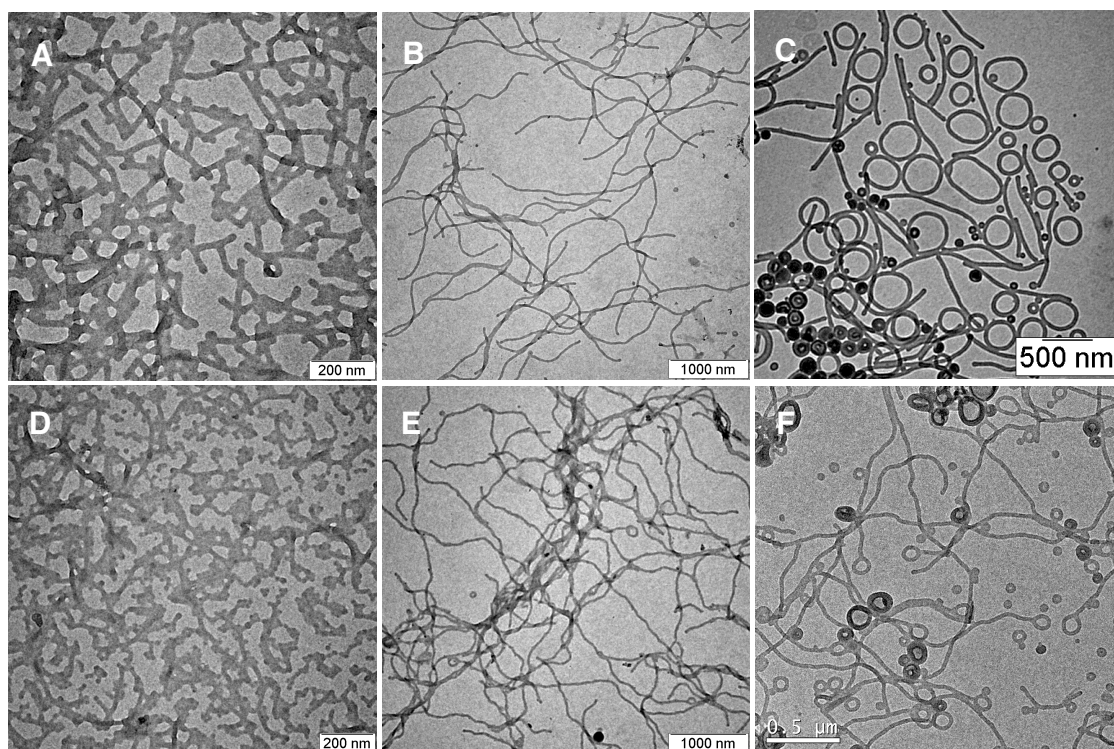


Fig S4. TEM images of micelles of (A) 3(PEG₂₂)-PS₁₂₀, (B) 3(PEG₂₂)-PS₁₅₂, (C) 3(PEG₂₂)-PS₁₇₁, (D) 9(PEG₇)-PS₁₂₁, (E) 9(PEG₇)-PS₁₅₀, (F) 9(PEG₇)-PS₁₆₆. All micelle solutions were prepared from a dioxane solution (0.5 wt %) of a block copolymer.

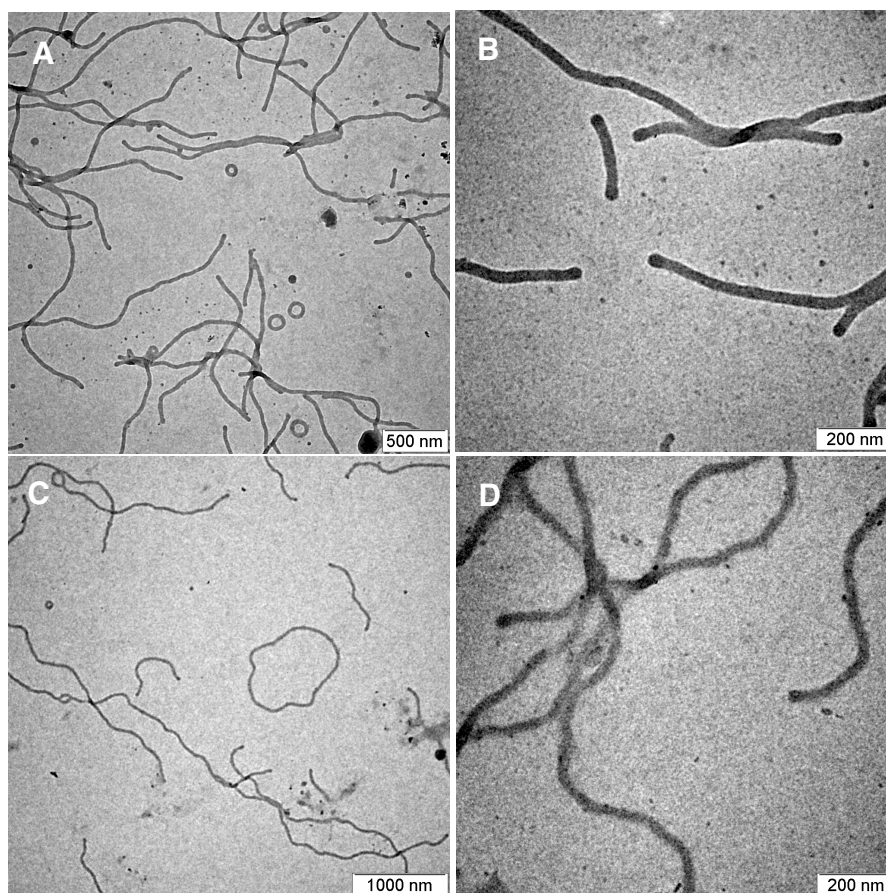


Fig. S5. Representative TEM images of cylindrical micelles prepared from the dioxane solution (0.5 wt %) of **3(PEG₂₂)-PS₁₅₂** (A and B) and **9(PEG₇)-PS₁₅₀** (C and D).

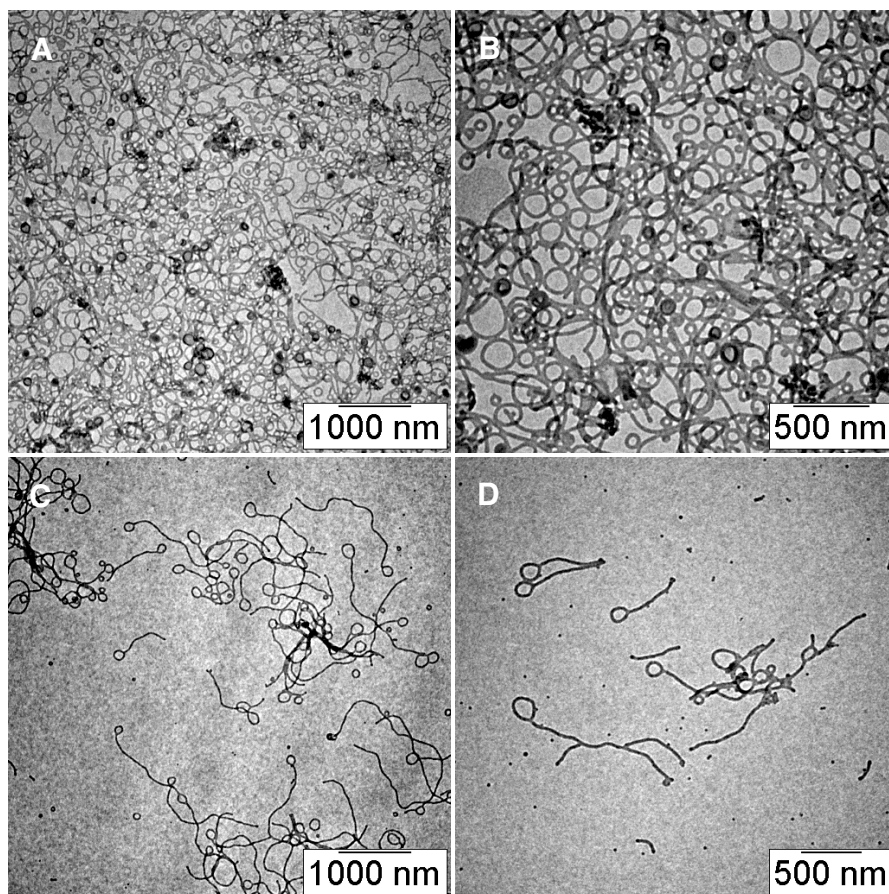


Fig. S6. Representative TEM images of cylindrical micelles of **3(PEG₂₂)-PS₁₅₂** (A and B) and lasso micelles of **9(PEG₇)-PS₁₅₀** (C and D). The micelle solutions were prepared from the dioxane solution (0.05 wt %) of a block copolymer.

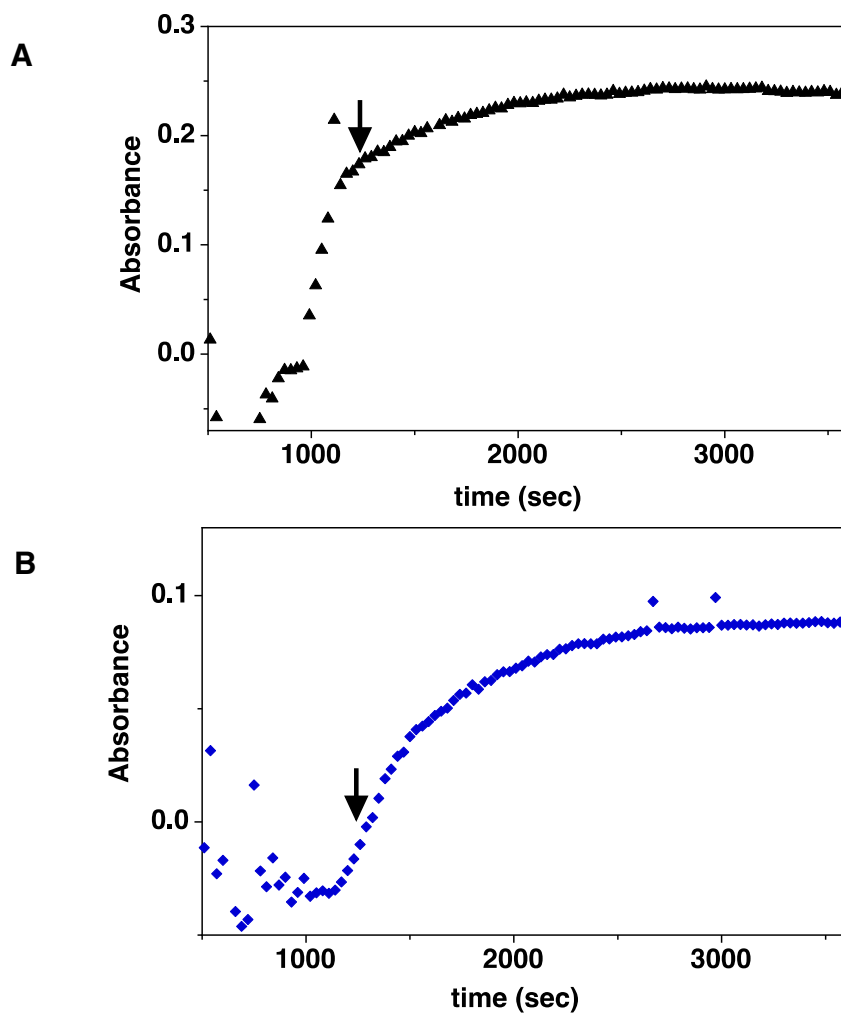


Fig. S7. Absorbance change of the dioxane solution (0.5 wt %) of **3(PEG₂₂)-PS₁₅₂** (A) and **9(PEG₇)-PS₁₅₀** (B) during water addition. The arrow indicates the water content of 25 %.

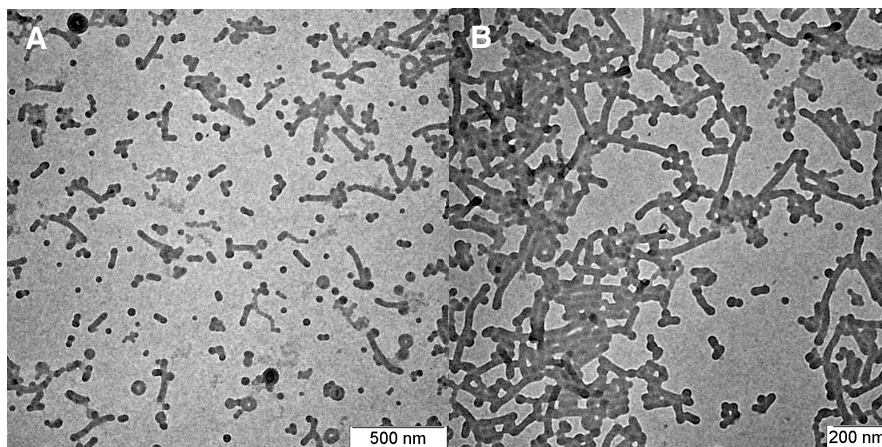


Fig. S8. Representative TEM images of the micelle solutions of **3(PEG₂₂)-PS₁₅₂** quenched at the water content of 25 %.

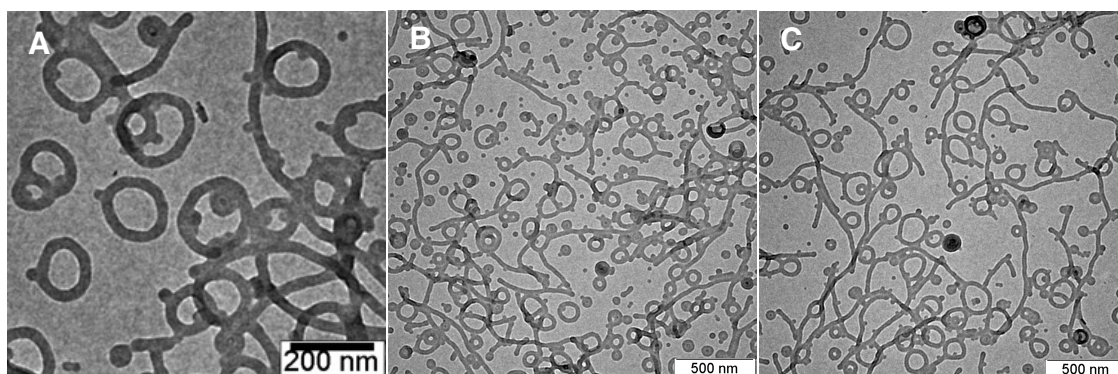


Fig. S9. Representative TEM images of the micelle solutions of **9(PEG₇)-PS₁₅₀** quenched at the water content of 25 %.

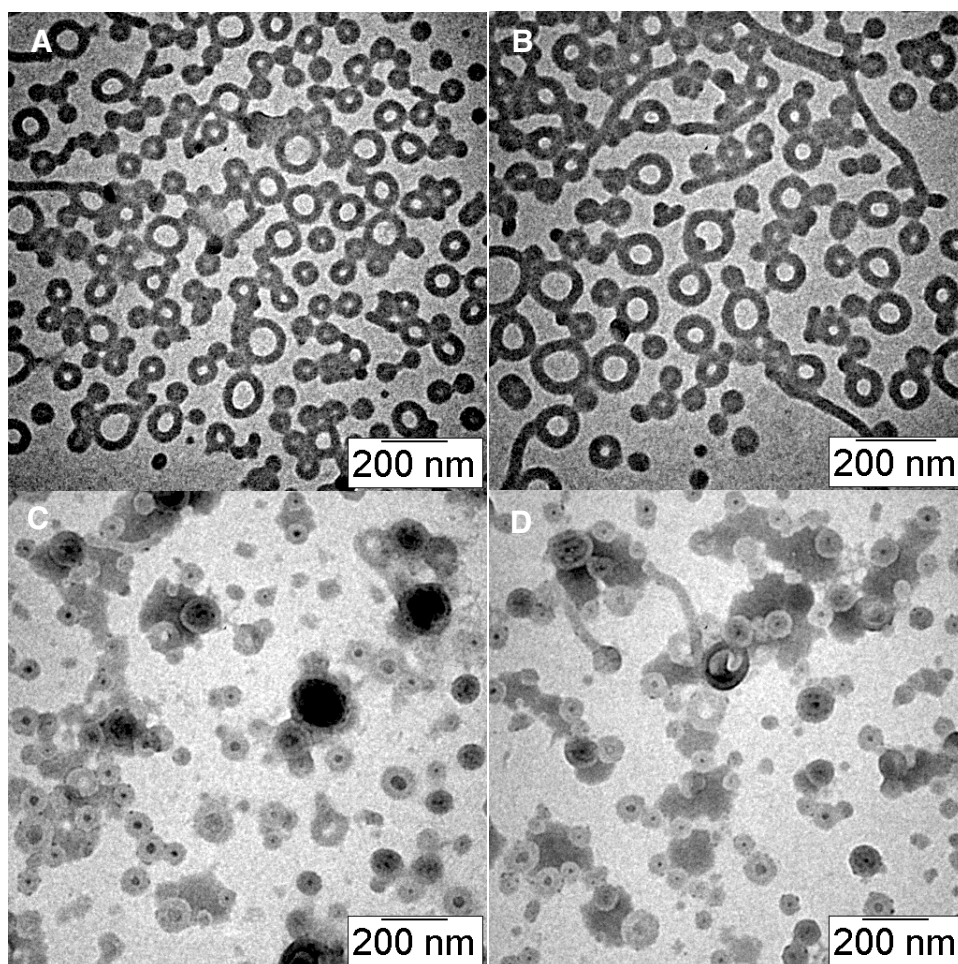


Fig. S10. Representative TEM images of toroidal micelles prepared from the dioxane solution (0.05 wt %) of $\text{PEG}_{68}\text{-PS}_{153}/9(\text{PEG}_7)\text{-PS}_{150}$. C and D are negatively stained TEM images.

References

1. (a) Oar, M. A.; Serin, J. M.; Dichtel, W. R.; Fréchet, J. M. J.; Ohulchanskyy, T. Y.; Prasad, P. N. *Chem. Mater.* 2005, 17, 2267. (b) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, 118, 9855.
2. Kim, K. T.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; van Hest, J. C. M. *Adv. Mater.* **21**, 2787-2791 (2009).