

Electronic Supporting Information

Self-Assembly of Polymeric Micelles into Complex but Regular Superstructures Based on Highly Controllable Core-Core Fusion between the Micelles

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S1 Experimental Section

S1.1 Materials

Poly(ethylene glycol) monomethyl ether (PEG₁₁₃-OH, $M_n=5000$ g/mol), 2-bromoisobutyryl bromide (98%) were purchased from Aldrich and used as received. Dichloromethane (CH₂Cl₂), triethylamine (TEA), 2-propanol and butanone were dried over CaH₂ and purified by distillation. 4-(Dimethylamino)pyridine (DMAP) was recrystallized in ethanol. CuCl was washed with acetic acid and methanol twice respectively to remove impurities. 4-Vinylpyridine (4VP) was dried over CaH₂ and distilled under reduced pressure. Azodiisobutyronitrile (AIBN) was purchased from Sinopharm Chemical Reagent Co. Ltd. and used after recrystallization in ethanol twice. All other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

S1.2 Methods

The ¹H NMR spectra were recorded on a Bruker DMX500 spectrometer in deuterated solvents.

The gel permeation chromatography (GPC) measurements were conducted with a Waters Breeze 1515 GPC analysis system using DMF as eluent.

Hydrodynamic radius $\langle R_h \rangle$ and size distribution of micelles were determined by dynamic light scattering (DLS) using a modified commercial light-scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- τ digital time correlator and ADLAS DPY425II solid-state laser (output power = 22 mW; $\lambda = 632.8$ nm). Before each measurement, sample solution was filtered through a 0.45 μ m Millipore filter (hydrophilic Millex-LCR, PTFE) to remove dust. Data was collected at a fixed scattering angle of 90° for 5 minutes at room temperature and analyzed by CONTIN fitting to obtain $\langle R_h \rangle$ and size distribution.

Transmission Electron Microscope (TEM) observations were conducted on a Philips CM120 electron

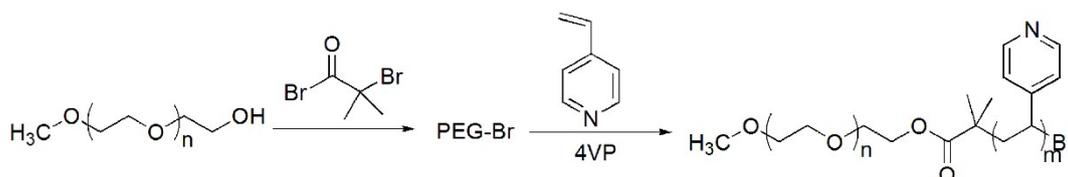
microscope at an acceleration voltage of 80 kV. Samples for TEM observations were prepared by depositing a drop of the aqueous suspensions onto a carbon-coated copper grid. TEM staining was performed by exposing samples to the vapor of RuO_4 for 120 min, which was produced by using 30 mg RuO_2 powder dissolved in 40 mL saturated sodium periodate aqueous solution in a closed vessel. Field-Emission Scanning Electron Microscope (FE-SEM) images were taken on Zeiss Ultra 55 FE-SEM. Samples were observed directly without gold deposition.

Fluorometry was conducted using an Edinburgh FLS 920 spectrometer equipped with an integrating sphere covering a wide range of wavelengths (200–800 nm).

Atomic Force Microscopy (AFM) was performed on a Bruker Multimode 8 microscope using a Tapping-Air mode. The samples were prepared by depositing the suspension on freshly cleaved mica surfaces.

UV-vis spectra were collected on a SHIMADZU-2550 spectrophotometer with 10 mm quartz cuvette.

S1.3 Synthesis of poly(ethylene glycol)-*b*-poly(4-vinylpyridine) (EV)^{1,2}



Scheme S1 Synthesis of poly(ethylene glycol)-*b*-poly(4-vinylpyridine) (PEG-*b*-P4VP) (EV).

Synthesis of PEG-Br macroinitiator¹

PEG₁₁₃-Br macroinitiator was synthesized by esterification of PEG₁₁₃-OH with 2-bromoisobutyryl bromide. PEG₁₁₃-OH (20 g, 4.0 mmol) was dissolved in 50 mL dried toluene at the presence of TEA (0.87 mL, 6.0 mmol) in a round-bottom flask. After cooling down to 0 °C in an ice-water bath, 2-bromoisobutyryl bromide (1.24 mL, 10.0 mmol) was slowly added and the reaction was allowed to proceed overnight. After filtration to remove the insoluble salts, the reaction solution was concentrated by rotary evaporation and precipitated into cold diethyl ether. The obtained powder was dried under vacuum overnight. The powder was then dissolved in NaOH solution at a pH between 8 and 9, and the solution was extracted twice by CH_2Cl_2 . The CH_2Cl_2 phase was kept and dried by anhydrous MgSO_4 under stirring, followed by filtration. The filtrate was concentrated and precipitated into cold diethyl ether twice, and dried under vacuum.

Synthesis of PEG-*b*-P4VP (EV)²

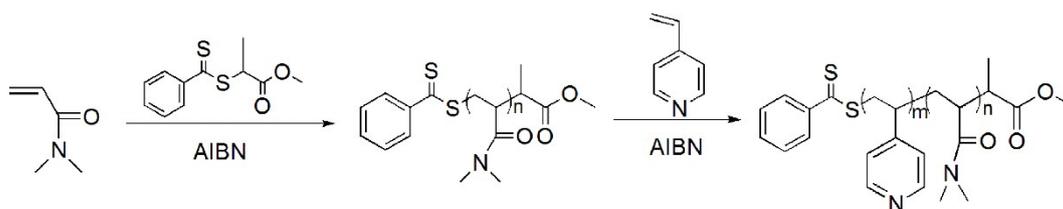
EV was synthesized by atom transfer radical polymerization. Polymerization of 4VP (8 mL, 75 mmol) was carried out in butanone (3.5 mL) and 2-propanol (1.5 mL) mixture solvent using PEG-Br (2.0 g, 0.4 mmol) as the macroinitiator at the presence of CuCl (0.05 g, 0.5 mmol) and tris-[2-(dimethylamino)

ethyl]amine (Me₆TREN) (0.14 mL, 0.5 mmol) after three freeze-thaw cycles. The polymerization was conducted at 45 °C for 8 h. The reaction was quenched by liquid nitrogen and diluted with CH₂Cl₂. The resultant polymer solution was filtered through a column filled with neutral alumina to remove the copper complex, then precipitated twice in cold diethyl ether and dried under vacuum overnight.

Synthesis of 5(6)-carboxyfluorescein modified PEG-*b*-P4VP (EVf)

5(6)-carboxyfluorescein (0.5 g, 1.3 mmol) was dissolved in 40 mL dried CH₂Cl₂. 2-bromoethanol (150 μL, 2.1 mmol) was then added to the solution followed by DIC (330 μL, 2.1 mmol) and DMAP (6.5 mg, 0.05 mmol). The mixture was stirred overnight at room temperature before it was filtered and added to excess diethyl ether to precipitate fluorescein-Br. Fluorescein-Br obtained above was reacted with EV by undergoing quaternization. Fluorescein-Br (6.86 mg, 14.2 μmol) along with EV (0.1 g, 4.6 μmol) were dissolved in 20 mL CH₃OH and stirred for 96 h. Then the solution was precipitated twice in cold diethyl ether and dried under vacuum.

S1.4 Synthesis of poly(*N,N*-dimethylacrylamide)-*b*-poly(4-vinylpyridine) (MV)^{3,4}



Scheme S2 Synthesis of poly(*N,N*-dimethylacrylamide)-*b*-poly(4-vinylpyridine) (MV).

Synthesis of poly(*N,N*-dimethylacrylamide) (PDMA)

PDMA-*b*-P4VP was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. PDMA block was synthesized by using 2-(methoxy carbonyl) ethyl disulfide benzyl ester (MCEDB, prepared in our laboratory⁵) as chain transfer agent (CTA). During the synthesized of PDMA, AIBN (14.7 mg, 0.09 mmol), MCEDB (98 μL, 0.45 mmol), DMA (6 mL, 58.2 mmol) and 6.0 mL dioxane were mixed together and then the mixture was degassed via three freeze-thaw cycles. The polymerization was conducted at 60 °C for 8 h.

After reaction, the mixture was diluted by dioxane and PDMA-CTA was purified through three cycles of dissolution in dichloromethane/precipitation in cold ethyl ether.

Synthesis of PDMA-*b*-P4VP (MV)

For synthesis of the P4VP block, PDMA-CTA (0.5 g, 0.095 mmol), AIBN (3.0 mg, 0.018 mmol), 4-vinylpyridine (2 mL, 18.8 mmol) and 6.0 mL dioxane were mixed and then the mixture was degassed *via* three freeze-thaw cycles. The reaction was conducted at 65 °C for 15 h. The product was purified by three cycles of dissolution in dichloromethane/precipitation in cold ethyl ether.

Synthesis of rhodamine B modified PDMA-*b*-P4VP (MVr)

Rhodamine B (0.5 g, 1.05 mmol), 2-bromoethanol (150 μ L, 2.1 mmol), DIC (330 μ L, 2.1 mmol), DMAP (6.5 mg, 0.053 mmol) and 40 mL CH_2Cl_2 were added in a round-bottom flask in sequence. The reaction was conducted at room temperature in dark for 15 h. After reaction, the mixture was purified by column chromatography using water/methanol mixture solvent at volume ratio of 4/1 as mobile phase. The resultant solution was concentrated and then precipitated twice in cold diethyl ether and dried under vacuum at room temperature to obtain rhodamine B bromide (rhodamine-Br).

MV (100 mg, 5.6 μ mol) and 7.97 mg rhodamine-Br were dissolved in 20 mL methanol and stirred at room temperature for 96 h in dark. The solution was precipitated in cold diethyl ether and dried under vacuum.

S1.5 Preparation of EV, MV and EV/MV block copolymer micelles

For the preparation of EV micelles or MV micelles, 25 mg copolymer (EV or MV) was firstly dissolved in 5 mL common solvent methanol. Then, water was added drop wise under stirring at a rate of 1.8 mL/h until the CH_3OH /water volume ratio reached 1/4. In the final suspension, the concentration of the copolymers was 1 mg/mL.

For the preparation of EV/MV block copolymer micelles, 12.5 mg EV and 12.5 mg MV were sufficiently dissolved in 5 mL common solvent methanol firstly. Then, 20 mL water was added drop wise under stirring at a rate of 1.8 mL/h.

S1.6 Preparation of EV, MV and EV/MV worm-like micelles

A 25 mL round-bottom flask was filled with 5 mL as-obtained micelle suspension with a syringe needle inserting into the liquid. *Worms* (abbr. for worm-like micelles, as indicated in the main text) were formed by pumping Ar through the needle into the suspension at 65 $^{\circ}\text{C}$ for 1 h (Fig. S3).

S1.7 Preparation of EVM-np and MVM-np octopus-like aggregates

After complete dissolution of 25 mg EV (or MV) and 17.2 mg Np in 5 mL methanol, 20 mL water was added drop wise into the mixture. Then, temperature of the suspension was set at 65 $^{\circ}\text{C}$, followed by purging Ar into the suspension at this temperature for 1 h (Fig. S3).

S2 Characterizations of Products

S2.1 Characterizations of EV, MV

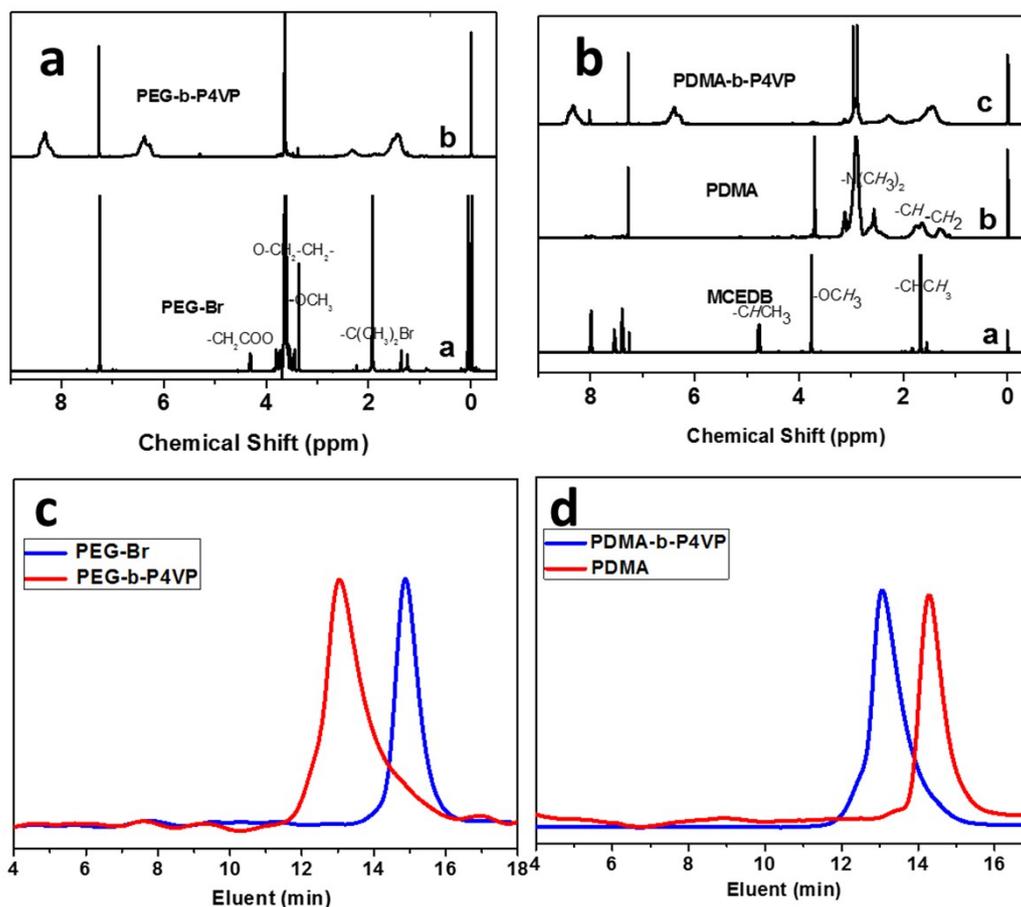


Fig. S1 ^1H NMR spectra (a, b) and GPC curves (c, d) of the macroinitiators and the block copolymers. Calibration for the GPC measurements was achieved using a series of monodisperse poly(ethylene oxide) standards.

S2.2 Characterizations of morphology of EV, MV and EV/MV spherical micelles

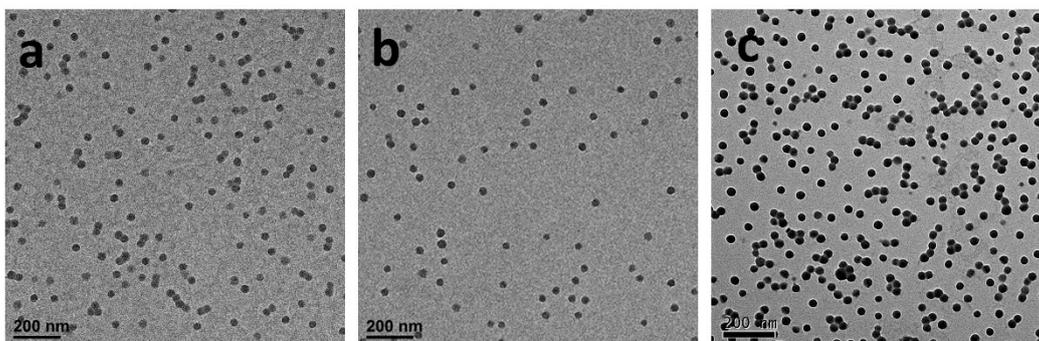


Fig. S2 TEM images of EV (a), MV (b) and EV/MV (c) spherical micelles in methanol/water (1/4, V/V) mixture solvent. Concentration of block copolymer in each of the suspensions is 1 mg/mL.

S2.3 The equipment for preparing worms



Fig. S3 The equipment for purging Ar into the suspensions at 65 °C and at the speed of 0.1 L/min.

S2.4 Characterizations of EV worms

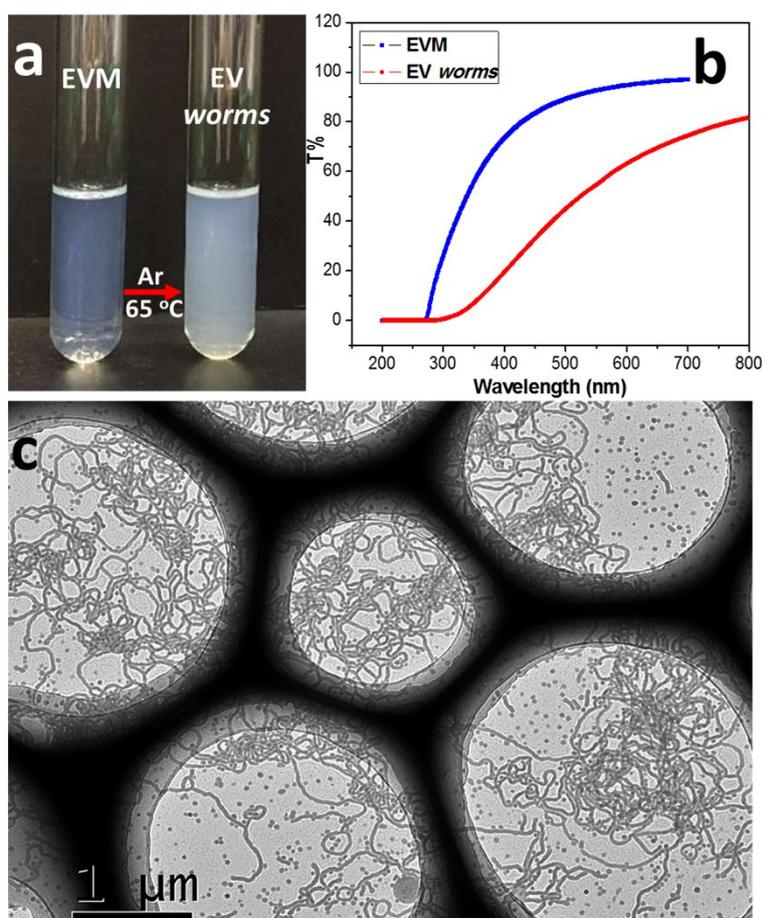


Fig. S4 (a) Photograph of the EVM and EV worms. (b) The percent transmittances of the EVM and EV

worms suspensions at different wavelengths of the incident light. (c) TEM image of the EV worms. The viscosity of EV worms suspension is 1.30 mPa s, according to repeated measurements by HAAKE MARS III rotary rheometer with a shear rate of 5.0 s^{-1} at $25 \text{ }^\circ\text{C}$.

S2.5 Control experiments to confirm that both the relatively high temperature ($65 \text{ }^\circ\text{C}$) and flexibility of the core are necessary for the morphological transition

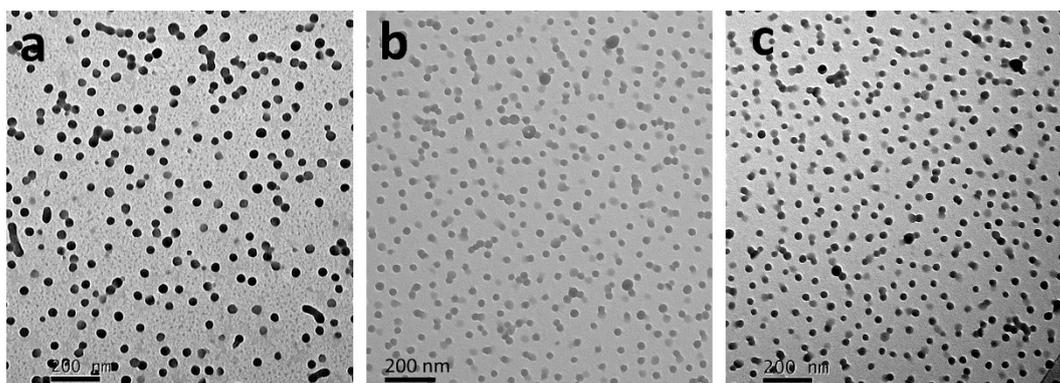


Fig. S5 TEM images of EV aggregates obtained by: (a) dialysis of suspension of the EV micelles against pure water for 96 h; (b) purging Ar into suspension of the EV spherical micelle at room temperature for 1 h; (c) heating the suspension of the EV spherical micelle at $65 \text{ }^\circ\text{C}$ for 1 h without the Ar purging.

S2.6 Characterizations of morphology of EVM/MVM spherical micelles and worms

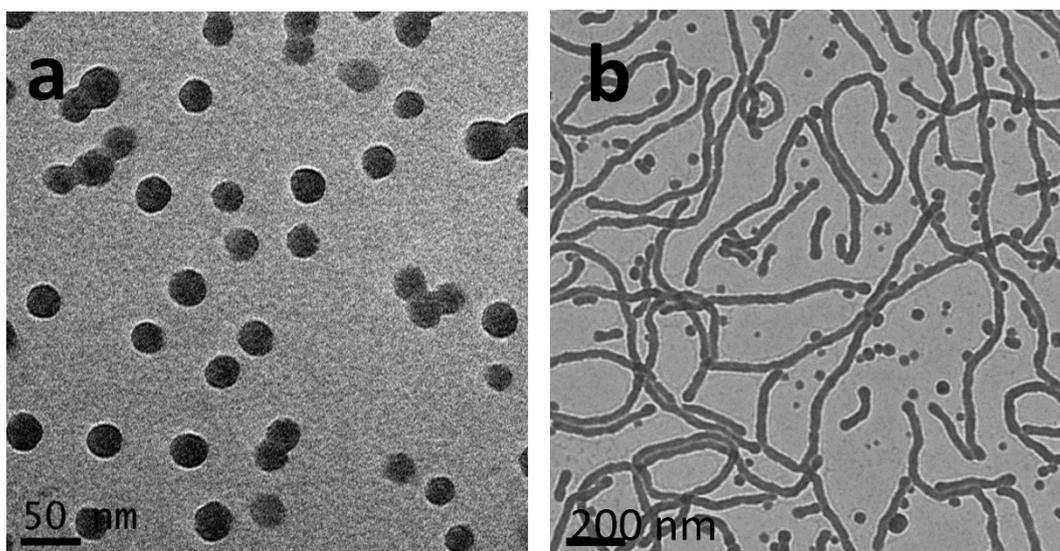


Fig. S6 TEM images of the aggregates formed in suspension of the EVM/MVM system: (a) the aggregates observed immediately after the mixing, and (b) the aggregates formed in the EVM/MVM system after the methanol evaporation.

S2.7 Characterizations of molar ratios of fluorescein/EVf and rhodamine B/MVr

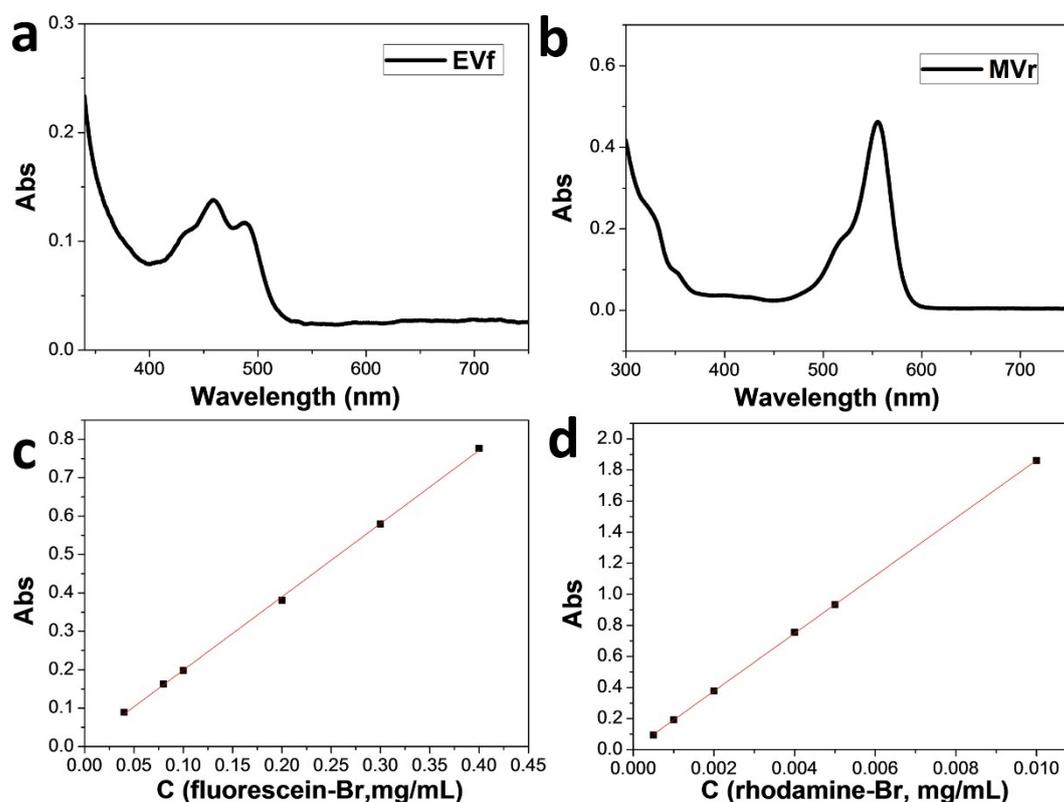


Fig. S7 UV-vis spectra of EVf (a) and MVr (b) solutions in methanol at the concentrations of 5.0 mg/mL and 0.5 mg/mL, respectively (it was confirmed that EVf and MVr were molecularly solubilized in methanol); the standard curves of fluorescein-Br (c, taken at 490 nm) and rhodamine-Br (d, taken at 551 nm) solubilized in methanol.

S2.8 Brief explanation of FRET

It is known that, in a system containing both donor and acceptor, when the distance between the donor and the acceptor pair is less than 10 nm, FRET will occur.⁶⁻⁸ Since the FRET efficiency exhibits a negative correlation with the distance, it can reflect the mixing extent between the donor-containing component and the acceptor-containing component, which makes FRET a very useful tool for investigation of phase separation structures in multi-component polymeric systems.⁸ Obviously, in the present study, FRET efficiency between fluorescein and rhodamine B can be utilized to characterize the mixing extent and the phase separation structure of the two block copolymers in the two *worms*.

S2.9 Shorter EV *worms* obtained by ultrasonically breaking the long EV *worms*

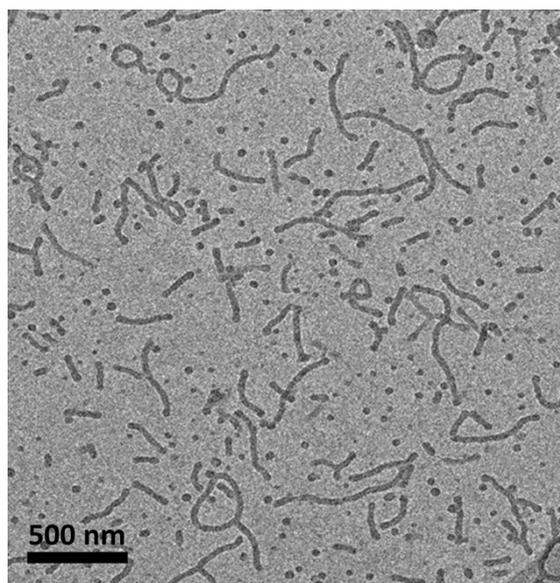


Fig. S8 TEM image of the shorter EV worms formed by ultrasonically breaking the long EV worms.

S2.10 Characterizations of size and morphology of EVM-np and MVM-np spherical micelles

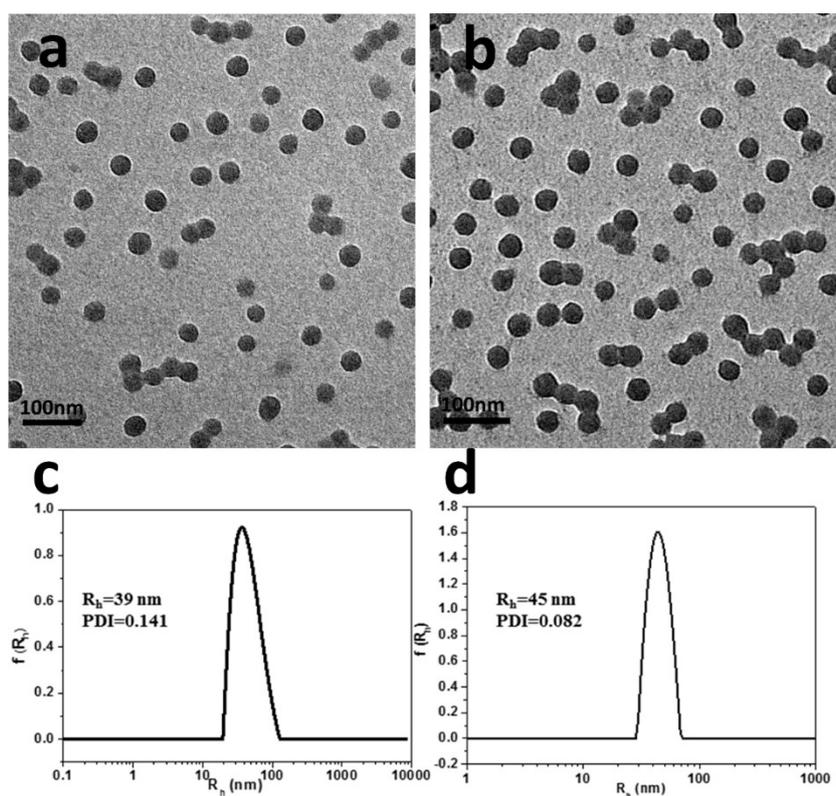


Fig. S9 TEM images and DLS curves of the EVM-np spherical micelles (a, c) and those of the MVM-np (b, d) spherical micelles formed in methanol/water (1/4, V/V). Concentration of block copolymer in each of the suspensions is 1 mg/mL.

S2.11 Tracking the EVM-np aggregates during the methanol evaporation

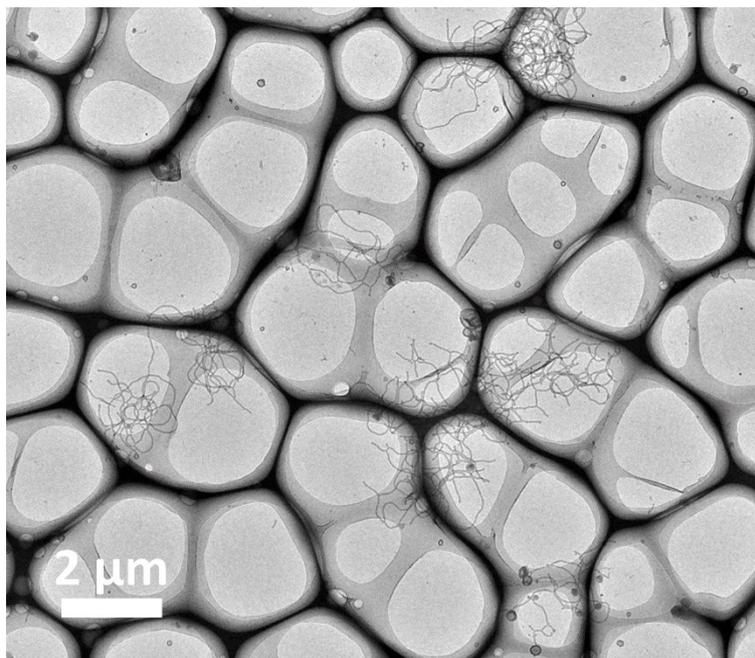


Fig. S10 TEM image of EVM-np aggregates formed at the early stage of the methanol evaporation.

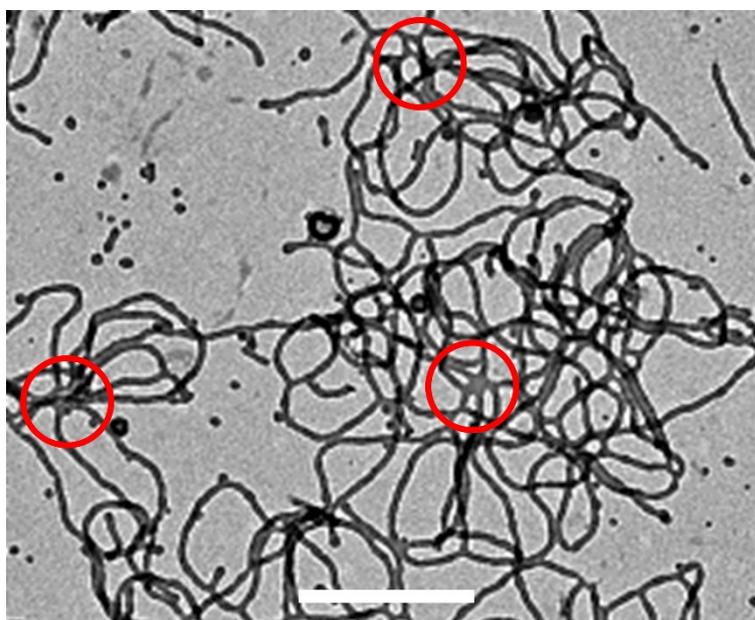


Fig. S11 TEM image of EVM-np aggregates formed at the early stage of the methanol evaporation.

Scale bar: 2 μm.

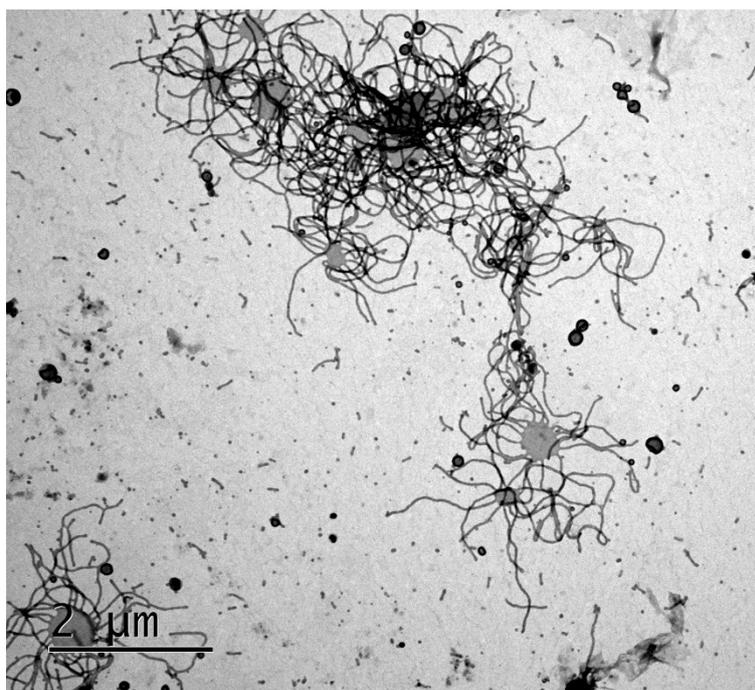


Fig. S12 TEM image of the freeze dried EVM-np octopus-like aggregates.

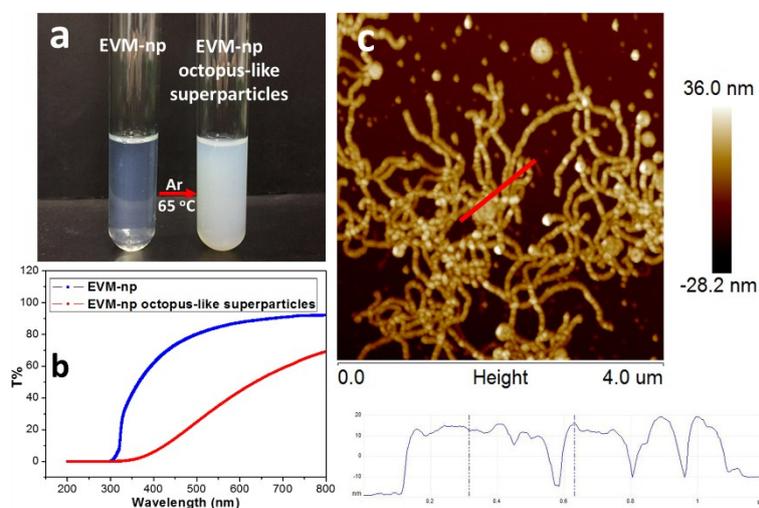


Fig. S13 (a) Photograph of the EVM-np and EVM-np octopus-like superparticles. (b) The percent transmittances of the EVM-np and EVM-np octopus-like superparticles suspensions at different wavelengths of the incident light. (c) AFM image of the EVM-np octopus-like superparticles. The viscosity of EVM-np octopus-like superparticles suspension is 1.80 mPa s, according to repeated measurements by HAAKE MARS III rotary rheometer with a shear rate of 5.0 s^{-1} at 25 °C.

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