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Supporting Information For
Self-Seeding of Block Copolymers with a π -Conjugated Oligo(*p*-phenylenevinylene) Segment: A Versatile Route toward Monodisperse Fiber-like Nanostructures

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SUPPORTING EXPERIMENTAL DETAILS

Materials

Methanol ($\geq 99.9\%$, Aldrich), ethanol ($\geq 99.8\%$, Aladdin) and isopropanol ($\geq 99.9\%$, Aldrich) were used as received for self-assembly experiments. *N*-isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized from a mixture of benzene and *n*-hexane (v:v = 1:3). 2-(Diethylamino)ethyl methacrylate (DEAEMA, Aldrich, 97%) was passed through a basic alumina column and distilled under reduced pressure from CaH_2 prior to use. Copper(I) chloride (CuCl , Aldrich, 99%) was purified by stirring overnight over $\text{CH}_3\text{CO}_2\text{H}$ at room temperature, followed by washing the solid with ethanol, diethyl ether and acetone prior to drying *in vacuo* at 40°C overnight. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN , Aldrich, 97%) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%) were used as received without further purification. The alkyne-terminated oligo(*p*-phenylenevinylene) was prepared according to our previous report.¹

Polymer Synthesis

Synthesis of azide-terminated poly(*N*-isopropylacrylamide)

A series of azide-terminated PNIPAM polymers with different chain lengths was prepared by ATRP using an azide-containing initiator in DMF/water at 25°C . The chain lengths were tailored by the feeding ratios of NIPAM-to-initiator (Scheme S1). In a typical procedure, a mixture of DMF/water (6 mL, v/v = 1:1), NIPAM (1.50 g, 13.26 mmol), CuCl (30 mg, 0.30 mmol) and

Me₆TREN (69 mg, 0.30 mmol) were introduced into a Schlenk tube. The flask was degassed by three cycles of freezing-pumping-thawing, then the azido-functionalized initiator of 2-(2-azidoethoxy) ethylbromoisobutyrate (83 mg, 0.30 mmol) was injected into the Schlenk tube to initiate the polymerization. The polymerization lasted 10 h at room temperature, and it was terminated by putting the flask into liquid N₂ and exposing the reaction mixture to air. The sample was passed through a short Al₂O₃ column to remove the residual catalyst. The reaction mixture was precipitated into cold *n*-hexane. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 0.70 g of white solid, PNIPAM₄₉-N₃. The polymer was subjected to GPC analysis (Figure S2). The average degree of polymerization (DP = 49) was determined by ¹H NMR (Figure 1) after coupling with OPV₅ on the basis of the predetermined *DP*_n of OPV₅.

GPC: $M_n^{\text{GPC}} = 6,200$ g/mol, $M_w/M_n = 1.12$.

¹H NMR (400 MHz, CDCl₃): δ (ppm): (4H, N₃CH₂CH₂OCH₂CH₂O₂C as the reference): 0.80-2.75 (9H, CH₂CHCONHCH(CH₃)₂), 3.44 (2H, N₃CH₂CH₂OCH₂CH₂O₂C), 3.67 (4H, N₃CH₂CH₂OCH₂CH₂), 4.00 (1H, CH₂CHCONHCH(CH₃)₂), 4.24 (2H, N₃CH₂CH₂OCH₂CH₂O₂C), 6.60-7.00 (1H, CH₂CHCONHCH(CH₃)₂).

Synthesis of azide-terminated poly(2-(diethylamino)ethyl methacrylate)

DEAEMA (2.00 g, 10.80 mmol), CuCl (54 mg, 0.54 mmol), HMTETA (124 mg, 0.54 mmol) and 2 mL of anhydrous THF were introduced into a Schlenk tube. The flask was degassed by three cycles of freezing-pumping-thawing, then the azide-functionalized initiator of 2-(2-azidoethoxy)

ethylbromoisobutyrate (75 mg, 0.27 mmol) was injected into the Schlenk tube to initiate the polymerization (Scheme S3). The polymerization lasted 10 h at room temperature and it was terminated by putting the flask into liquid N₂. The sample was passed through a short Al₂O₃ column to remove the residual catalyst. The reaction mixture was precipitated into cold *n*-hexane. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 0.62 g of white solid, PDEAEMA₆₀-N₃, which was subjected to GPC analysis (Figure S19). The average degree of polymerization (DP = 60) was determined by ¹H NMR (Figure S18) after coupling with OPV₅ on the basis of the predetermined *DP*_n OPV₅.

GPC: $M_n^{\text{GPC}} = 5,800 \text{ g/mol}$, $M_w/M_n = 1.16$.

¹H NMR (400 MHz, CDCl₃): δ (ppm): (4H, N₃CH₂CH₂OCH₂CH₂O₂C as the reference): 0.80-1.78 (11H, CH₂C(CH₃)CO₂CH₂CH₂N(CH₂CH₃)₂), 2.57 (4H, CH₂C(CH₃)CO₂CH₂CH₂N(CH₂CH₃)₂), 2.69 (2H, CH₂C(CH₃)CO₂CH₂CH₂N(CH₂CH₃)₂), 3.44 (2H, N₃CH₂CH₂OCH₂CH₂O₂C), 3.67 (4H, N₃CH₂CH₂OCH₂CH₂), 3.99 (2H, CH₂C(CH₃)CO₂CH₂CH₂N(CH₂CH₃)₂), 4.22 (2H, N₃CH₂CH₂OCH₂CH₂O₂C).

Synthesis of OPV₅-*b*-PNIPAM₁₈, OPV₅-*b*-PNIPAM₄₉, OPV₅-*b*-PNIPAM₇₅ and OPV₅-*b*-PDEAEMA₆₀ diblock copolymers

The Cu-catalyzed alkyne azide cycloaddition (CuAAC) reaction between azide-terminated homopolymer and alkyne-terminated OPV₅ was used to synthesize the diblock copolymers (Schemes S2 and S3, Figures 1, S3, S18 and S19, and Table 1) as described in our previous work.¹

In a typical procedure, alkyne-terminated OPV₅ (40 mg, 0.025 mmol), PNIPAM₄₉-N₃ ($M_{n, GPC}$ = 6,200 g/mol, M_w/M_n = 1.12, 250 mg, 0.037 mmol), CuCl (7.5 mg, 0.075 mmol) and HMTETA (20 μ L, 0.075 mmol) were added into a 25 mL Schlenk flask (flame-dried under vacuum prior to use). 5 mL of dry THF was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 40°C. Then the reaction was allowed to stir for 2 days. Aliquots of the mixture were removed to monitor the reaction progress by GPC (Figure S3). The solvent was evaporated and the residue was purified by silica column chromatography (eluent: CH₂Cl₂/methanol = 10/1) to remove the unreacted alkyne-terminated OPV₅ and catalyst. The crude product was then purified by repeated dissolution in THF and precipitation in cold water three times in order to remove the unreacted PNIPAM₄₉-N₃, followed by drying *in vacuo* overnight to give 110 mg of yellow solid (yield: 62 %), OPV₅-*b*-PNIPAM₄₉. The polymer was subjected to GPC analysis (Figure S3). The molecular weight was determined by ¹H NMR on the basis of the predetermined DP_n of OPV₅ (Figure 1).

INSTRUMENTATION

¹H (400 MHz) NMR analyses were performed on a JEOL JNM-ECZ400 spectrometer in CDCl₃ and CD₂Cl₂, tetramethylsilane was used as internal standard. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) using a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, a Waters 2487 dual λ absorbance detector and a

set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000) and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μ m). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF)

Small aliquots of sample solutions (2 μ L, 1.0 mg/mL) in CH₂Cl₂ were added to a sample plate for MALDI-TOF. After drying in air at room temperature (~10 min), an aliquot of α -cyano-4-hydroxy cinnamic acid (2 μ L, 5.0 mg/mL) dispersed in a mixture of CH₃CN and water (CH₃CN/water = 1/1) was added and allowed to dry in air at room temperature. MALDI-TOF spectra were obtained on a Waters MICROMASS MALDI micro MX Mass Spectrometer.

Transmission electron microscopy (TEM)

TEM images were obtained by a JEOL JEM-2100 instrument operated at 80 kV. A drop of micellar solution (10 μ L) was placed on a Formvar and carbon-coated copper grid for 30 s and then a filter paper was touched to the edge of the drop to absorb most of the liquid on the grid. The grid was allowed to dry at room temperature. For the samples stained by phosphotungstic acid, after the grid was dried (*ca.* 1 min after touching it with the filter paper), a drop of phosphotungstic acid aqueous solution (10 μ L, 1.0 mg/mL) was added onto the surface. After 1 min, most of the solution on the grid was absorbed by touching the edge of the drop with a filter paper, and then the grid was allowed to dry at room temperature. For each sample, the length distributions of micelles

were determined by tracing more than 200 individual micelles, and width distributions were determined by making measurements at least 200 different positions on several micelles and analysis using the software program ImageJ from the National Institutes of Health (US). Values of the number-average length (L_n) and weight-average length (L_w) of micelles were calculated as follows:

$$L_n = \frac{\sum_{i=1}^N N_i L_i}{\sum_{i=1}^N N_i} \quad (1)$$

$$L_w = \frac{\sum_{i=1}^N N_i L_i^2}{\sum_{i=1}^N N_i L_i} \quad (2)$$

where N_i is the number of micelles of length L_i , and N is the number of calculated micelles in each sample. The distribution of micellar length is characterized by both L_w/L_n and the standard deviation of the length distribution σ .

Atomic force microscopy (AFM)

AFM images were acquired in air in tapping mode using a JPK NanoWizard Sense system. Aliquots (10 μ L) of micellar solutions prepared as described above were deposited on a mica substrate and dried at room temperature in air.

Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS measurements were run at BL14B1 of the Shanghai Synchrotron Radiation Facility. Samples of OPV₅-*b*-PNIPAM for GIWAXS experiments were prepared by casting micellar solution (1 mg/mL in ethanol) onto a silicon wafer and allowing the solvent to evaporate at room

temperature.

SELF-ASSEMBLY EXPERIMENTS

Self-assembly of OPV₅-*b*-PNIPAM and OPV₅-*b*-PDEAEMA₆₀ diblock copolymers in different alcoholic solvents

OPV₅-*b*-PNIPAM and OPV₅-*b*-PDEAEMA₆₀ were directly suspended in different alcoholic solvents. The mixture was heated at 80°C for 30 min (65°C for methanol), followed by aging at room temperature for 48 h. A drop of solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 2, S4, S5 and S20).

Preparation of seed fiber-like micelles of OPV₅-*b*-PNIPAM and OPV₅-*b*-PDEAEMA₆₀

Seed micelles were prepared by sonicating (BRANSON model 1510 70 W ultrasonic cleaning bath) at 0°C for different times the original long fiber-like micelles formed by the diblock copolymer. Seed micelles of OPV₅-*b*-PNIPAM₇₅ and OPV₅-*b*-PNIPAM₄₉ for self-seeding experiments were obtained by sonication for 30 min at 0°C, while those of OPV₅-*b*-PNIPAM₁₈ and OPV₅-*b*-PDEAEMA₆₀ were obtained by sonication for 3 h.. To obtain seed micelle solutions with different concentrations, the seed micellar solution of OPV₅-*b*-PNIPAM₄₉ in ethanol (0.1 mg/mL) was obtained by sonication for 30 min, followed by dilution with ethanol to obtain solutions with concentrations of 0.05 and 0.02 mg/mL.

Self-Seeding of OPV-*b*-PNIPAM with different annealing time

Aliquots of seed micelles (0.05 mg/mL in ethanol) of OPV₅-*b*-PNIPAM₄₉ and OPV₅-*b*-PNIPAM₁₈ were heated at 50°C for different times (15, 30, 60 90 and 120 min), allowed to cool in air, and then aged for 48 h. Then, a drop of each solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 4, S10 and S11, and Tables S1 and S2).

Self-Seeding of OPV₅-*b*-PNIPAM₄₉ in different solvents

Seed micelle samples of OPV₅-*b*-PNIPAM₄₉ were prepared by sonication at 0°C for 30 min in methanol, ethanol and isopropanol, respectively. These seed micelle solutions (0.05 mg/mL) were then heated at different temperatures (35°C to 60°C), followed by cooling in the air and aging for 48 h. Then, a drop of each solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figure 5, S12 and S13, and Tables S4 and S5).

Self-Seeding of OPV-*b*-PNIPAM₄₉ with different concentrations

The seed micelle solutions of OPV₅-*b*-PNIPAM₄₉ (0.1 mg/mL) in ethanol were diluted with ethanol to afford another two dilute seed micellar solutions with concentrations of 0.05 and 0.02 mg/mL. Aliquots of those seed solutions were heated at various temperatures (from 35°C to 60°C) for 30 min, followed by cooling and aging at room temperature for 48 h. Then, a drop of each solution was placed on a Formvar and carbon-coated copper grid and examined by TEM (Figures 6, S12, S14 and S15, Tables S4, S6 and S7).

Self-Seeding of OPV₅-*b*-PDEAEMA₆₀

Aliquots of a seed micelle solution (0.05 mg/mL in ethanol) were annealed at different temperature from 40°C to 60°C for 30 min and allowed to cool back to room temperature and age for 48 h. Then, a drop of each solution was placed on a Formvar and carbon-coated copper grid. The samples were stained with phosphotungstic acid and examined by TEM (Figures 8 and S21, and Table S10).

ADDITIONAL RESULTS AND DISCUSSION

The BCP OPV₅-*b*-PNIPAM₁₈ shows relatively complex self-assembly behavior in methanol. In addition to fiber-like micelles, platelet structures with fiber-like micelles protruding from the ends are found in TEM images (Figures 2A, 2B). Here we consider factors that might affect the formation of these 2D structures.

PFS BCPs form platelet micelles when the length of the corona-forming block is similar to, or shorter than, the PFS block.²⁻³ One explains the formation of fiber-like micelles in samples with longer corona chains in terms of repulsion of the solvent-swollen corona chains limiting lateral growth of the crystalline core. Other systems have also been reported to form 2D platelet-like structures with some protruding fibers from the ends. These include the direct self-assembly in isopropanol of PFS-*b*-P2VP with 6 mol% quaternization of the P2VP block,⁴ PCL-*b*-PEO/PCL in water⁵ and amphiphilic Pt(II) complexes with solubilized ancillary ligands based on PEO.⁶

On the basis of these results, we suggest that both the solvent and the chain length of PNIPAM

block play an important role in the formation of these 2D structures. We estimate the solubility parameters of OPV to be about $18.7 \text{ MPa}^{1/2}$, a value calculated as the solubility parameter of poly[2-methoxy-5(20-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). The solubility parameter of PNIPAM is $23.5 \text{ MPa}^{1/2}$, closer to the solubility parameter of isopropanol ($23.6 \text{ MPa}^{1/2}$) than to those of ethanol ($26.5 \text{ MPa}^{1/2}$) or methanol ($29.6 \text{ MPa}^{1/2}$) (Table 2).⁷⁻⁹ From this perspective, we infer that isopropanol is the best solvent for OPV-*b*-PNIPAM and methanol is the worst. In addition, we expect that the solubility of OPV-*b*-PNIPAM will be enhanced for molecules with longer PNIPAM blocks. .

For OPV₅-*b*-PNIPAM₁₈, characterized by $\bar{D} = 1.10$, there is a distribution in the lengths of the PNIPAM segments. We anticipate that when a hot solution of OPV₅-*b*-PNIPAM₁₈ in methanol is cooled, the OPV₅-*b*-PNIPAM₁₈ molecules with shorter PNIPAM blocks will tend to aggregate first upon cooling, due to their lower solubility, and undergo self-nucleation to form platelet micelles. The weak steric repulsion between the shorter PNIPAM corona chains promotes the formation of 2D structures that become elongated by epitaxial crystallization to reduce the interface between OPV segment and the solvent. In our view, upon further cooling and aging, the copolymer molecules of OPV₅-*b*-PNIPAM₁₈ with longer PNIPAM blocks are enriched in the sample and start to attach to the exposed face of micelles by crystallization. Both ends of formed platelet-like micelles serve as nucleation sites for epitaxial crystallization of these BCPs. However, under these conditions, the PNIPAM chains are longer, and the enhanced steric repulsion between the PNIPAM corona chains leads to the formation of fiber-like micelles. In this way, fiber-like structures grow from the ends of the platelet structures.

In ethanol and isopropanol, the solvophobic effect would become weaker for OPV₅-*b*-PNIPAM₁₈ due to the decrease in solubility parameter. These better solvents for PNIPAM promote swelling of the corona chains, and steric repulsion resists the lateral growth of the OPV core that would lead to platelet formation. Therefore, only fiber-like micelles were formed. This explanation implies that OPV₅-*b*-PNIPAM₁₈ occupies a delicate position that straddles a phase boundary between 1D and 2D structures, so that a change in solvency for the corona chains can lead to a change in morphology. Since the steric repulsion within the PNIPAM corona layer of micelles of OPV₅-*b*-PNIPAM₄₉ and OPV₅-*b*-PNIPAM₇₅ is much stronger than in micelles of OPV₅-*b*-PNIPAM₁₈, resulting from the increase in PNIPAM chain length, only fiber-like micelles were formed for OPV₅-*b*-PNIPAM₄₉ and OPV₅-*b*-PNIPAM₇₅.

SUPPORTING FIGURES

Feeding ratio of NIPAM to initiator 1: 22, 1: 44, 1: 88

Scheme S1. Synthesis of PNIPAM-N₃ with different chain lengths.

Figure S1. ¹H NMR spectra in CDCl₃ of PNIPAM-N₃ with different chain lengths.

Figure S2. GPC curves (RI detector) of PNIPAM-N₃ with different chain lengths in THF. Molecular weights were calculated with the help of polystyrene standards.

Scheme S2. Synthesis of OPV₅-*b*-PNIPAM diblock copolymers.

Figure S3. GPC curves of OPV₅, OPV₅-*b*-PNIPAM₁₈, OPV₅-*b*-PNIPAM₄₉ and OPV₅-*b*-PNIPAM₇₅ in THF. Molecular weights were determined by the use of polystyrene standards.

Figure S4. TEM images of micelles of OPV₅-*b*-PNIPAM₁₈ obtained in ethanol (A) and isopropanol (B), OPV₅-*b*-PNIPAM₄₉ obtained in ethanol (C) and isopropanol (D), OPV₅-*b*-PNIPAM₇₅ obtained in ethanol (E) and isopropanol (F) by heating at 80°C for 30 min (0.1 mg/mL), followed by cooling to room temperature for 48 h.

Figure S5. TEM images of fiber-like micelles of OPV₅-*b*-PNIPAM₁₈ (A), OPV₅-*b*-PNIPAM₄₉ (C) and OPV₅-*b*-PNIPAM₇₅ (E) in ethanol (0.1 mg/mL). Histograms of width distributions of fiber-like micelles of OPV₅-*b*-PNIPAM₁₈ (B), OPV₅-*b*-PNIPAM₄₉ (D) and OPV₅-*b*-PNIPAM₇₅ (F).

Figure S6. AFM height images and the height profiles along the red line of micelles formed by OPV₅-*b*-PNIPAM₁₈ (A), OPV₅-*b*-PNIPAM₄₉ (B) and OPV₅-*b*-PNIPAM₇₅ (C) in ethanol (0.05 mg/mL).

Figure S7. TEM images of fragmented micelles of OPV₅-*b*-PNIPAM₁₈ obtained by sonication for 1 h (A) and 2 h (B) at 0°C.

Figure S8. GPC curves (UV detector) of OPV₅ and OPV₅-*b*-PNIPAM₁₈ in THF before and after sonication for 3h.

Figure S9. GIWAXS spectra of dried OPV₅ and fiber-like micelles of OPV₅-*b*-PNIPAM₁₈, OPV₅-*b*-PNIPAM₄₉ and OPV₅-*b*-PNIPAM₇₅ in ethanol.

Figure S10. TEM images and contour length distribution histograms of fiber-like micelles of OPV₅-b-PNIPAM₄₉ obtained by annealing the seeds in ethanol (0.05 mg/mL) for 15 (A), 60 (B), 90 (C) and 120 (D) min at 50°C, followed by aging at room temperature for 48 h.

Figure S11. TEM images and contour length distribution histograms of fiber-like micelles of OPV₅-*b*-PNIPAM₁₈ obtained by annealing the seeds in ethanol (0.05 mg/mL) for 15 (A), 60 (B), 90 (C) and 120 (D) min at 50°C, followed by aging at room temperature for 48 h.

Figure S12. TEM images and contour length distribution histograms of the seeds of OPV₅-b-PNIPAM₄₉ (A) in ethanol (0.05 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G), 57°C (H) and 60°C (I) for 0.5 h, followed by aging at room temperature for 48 h.

Figure S13. TEM images and contour length distribution histograms of the seeds of OPV₅-*b*-PNIPAM₄₉ (A) in isopropanol (0.05 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G) and 57°C (H) for 30 min, followed by aging at room temperature for 48 h.

Figure S14. TEM images and contour length distribution histograms of the seeds of OPV₅-*b*-PNIPAM₄₉ (A) in ethanol (0.1 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G), 57°C (H) and 60°C (I) for 30 min, followed by aging at room temperature for 48 h.

Figure S15. TEM images and contour length distribution histograms of the seeds of OPV₅-*b*-PNIPAM₄₉ (A) in ethanol (0.02 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G) and 57°C (H) for 0.5 h, followed by aging at room temperature for 48 h.

Figure S16. TEM images and contour length distribution histograms of the seeds of OPV₅-*b*-PNIPAM₁₈ (A) in ethanol (0.1 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G), 57°C (H) and 60°C (I) for 0.5 h, followed by aging at room temperature for 48 h.

Figure S17. TEM images and contour length distribution histograms of the seeds of OPV₅-b-PNIPAM₇₅ (A) in ethanol (0.1 mg/mL) and micelles obtained after annealing the seed solution at 35°C (B), 40°C (C), 44°C (D), 47°C (E), 50°C (F), 53°C (G) and 57°C (H) for 30 min, followed by aging at room temperature for 48 h.

Scheme 3 Synthesis of OPV₅-*b*-PDEAEMA₆₀ diblock copolymer.

Figure S18. ¹H NMR spectrum of OPV₅-*b*-PDEAEMA₆₀ in CD₂Cl₂.

Figure S19. GPC curves of OPV₅, PDEAEMA₆₀, OPV₅-*b*-PDEAEMA₆₀ and the reaction solution before purification.

Figure S20. TEM image of fiber-like micelles obtained by heating the ethanol solution of OPV₅-*b*-PDEAEMA₆₀ (0.1 mg/mL) for 30 min, followed by cooling in the air and aging at room temperature for 48 h (B: higher magnification image of the grid shown in A).

Figure S21. TEM images and contour length distribution histograms of the seeds of OPV₅-*b*-PDEAEMA₆₀ (A) in ethanol (0.05 mg/mL) and micelles obtained after annealing the seed solution at 40°C (B), 45°C (C), 50°C (D), 53°C (E), 55°C (F), 57°C (G) and 60°C (H) for 30 min, followed by aging at room temperature for 48 h.

SUPPORTING TABLES

Table S1. Characteristics of fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ in ethanol (0.05 mg/mL) obtained by the self-seeding strategy when heated at 50°C for different times (15, 30, 60, 90 and 120 min), allowed to cool in air and then aged for 48 h^a

Time (min)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
15	210	223	1.06	52	0.25
30	292	310	1.06	73	0.32
60	323	339	1.05	74	0.34
90	281	298	1.06	71	0.34
120	288	302	1.05	67	0.34

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S2. Characteristics of fiber-like micelles of OPV₅-*b*-PNIPAM₁₈ in ethanol (0.05 g/mL) obtained by the self-seeding strategy when heated at 50°C for different times (15, 30, 60, 90 and 120 min), allowed to cool in air, and then aged for 48 h^a

Time (min)	L_n (nm)	L_w (nm)	L_w/L_n ^b	σ (nm) ^b	σ/L_n ^b
15	204	237	1.16	82	0.40
30	305	336	1.10	97	0.32
60	288	323	1.12	98	0.34
90	299	335	1.12	103	0.34
120	316	351	1.11	106	0.34

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviation of micelle length distribution, respectively, as calculated from the histograms of the length distributions.

Table S3. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by the self-seeding strategy in methanol (0.05 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n ^b	σ (nm) ^b	σ/L_n ^b
35	34	48	1.42	22	0.65
40	43	52	1.20	19	0.44
44	92	115	1.25	47	0.52
47	84	119	1.42	55	0.66
50	155	225	1.45	105	0.68
53	174	244	1.40	110	0.63

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S4. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by the self-seeding strategy in ethanol (0.05 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	44	56	1.27	22	0.50
35	74	80	1.08	22	0.39
40	103	109	1.06	25	0.24
44	150	161	1.07	41	0.27
47	172	184	1.07	45	0.26
50	292	310	1.06	73	0.25
53	391	411	1.05	87	0.22
57	581	610	1.05	130	0.22
60	1152	1279	1.11	379	0.33

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S5. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by the self-seeding strategy in isopropanol (0.05 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	52	59	1.14	19	0.37
35	62	69	1.11	21	0.34
40	80	86	1.08	22	0.28
44	94	107	1.14	35	0.37
47	203	219	1.08	56	0.28
50	311	330	1.06	79	0.25
53	625	669	1.07	164	0.26
57	1127	1217	1.08	330	0.29

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S6. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by the self-seeding strategy in ethanol (0.1 mg/mL).^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	44	56	1.27	22	0.50
35	51	55	1.08	15	0.29
40	78	82	1.05	17	0.22
44	126	135	1.07	33	0.26
47	134	142	1.06	31	0.23
50	205	221	1.08	57	0.28
53	334	354	1.06	80	0.24
57	536	606	1.13	196	0.37
60	1023	1125	1.10	326	0.32

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S7. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by the self-seeding strategy in ethanol (0.02 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	44	56	1.27	22	0.50
35	97	103	1.06	24	0.25
40	126	136	1.08	35	0.24
44	239	256	1.07	65	0.27
47	248	258	1.04	51	0.26
50	350	368	1.05	75	0.25
53	633	671	1.06	153	0.22
57	710	796	1.12	242	0.22

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S8. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₁₈ obtained by the self-seeding strategy in ethanol (0.1 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	40	45	1.13	15	0.38
35	51	57	1.12	18	0.35
40	75	83	1.10	24	0.32
44	113	129	1.14	42	0.37
47	173	194	1.12	60	0.35
50	263	287	1.09	77	0.29
53	359	381	1.06	94	0.26
57	503	548	1.09	149	0.30
60	762	815	1.07	199	0.26

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S9. Characteristics of the seed and fiber-like micelles of OPV₅-*b*-PNIPAM₇₅ obtained by the self-seeding strategy in ethanol (0.1 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	38	40	1.04	8	0.21
35	50	54	1.07	13	0.26
40	72	78	1.06	18	0.25
44	101	106	1.04	20	0.20
47	119	125	1.04	24	0.20
50	160	165	1.03	29	0.18
53	343	357	1.04	70	0.20
57	665	718	1.11	218	0.33

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

Table S10. Characteristics of the seed and elongated fiber-like micelles of OPV₅-*b*-PDEAEMA₆₀ obtained by the self-seeding in ethanol (0.05 mg/mL)^a

T (°C)	L_n (nm)	L_w (nm)	L_w/L_n^b	σ (nm) ^b	σ/L_n^b
seed	41	46	1.11	13	0.32
40	48	50	1.04	16	0.33
45	75	80	1.06	19	0.25
50	106	110	1.04	20	0.19
53	126	131	1.04	25	0.20
55	240	252	1.05	55	0.23
57	275	289	1.05	60	0.22
60	444	471	1.06	105	0.24

^a The lengths of fiber-like micelles were measured from their TEM images and the average values were obtained from over 200 readings.

^b L_n , L_w and σ are the number-average micelle length, weight-average micelle length, and the standard deviations of micelle length distributions, respectively, as calculated from the histograms of the length distributions.

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