SUPPORTING INFORMATION

Competitive Self-Assembly Kinetics as a Route to Control the Morphology of Core-Crystalline Cylindrical Micelles

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1. EXPERIMENTAL SECTION

1.1 Materials

The BCPs PFS_{35}-*b*-$P2VP_{400}$ and PFS_{26}-*b*-$PNIPAM_{520}$ (the subscripts refer to the number average degrees of polymerization) are the same samples reported in previous publications.[1,2] PFS_{26}-*b*-$PNIPAM_{190}$ was synthesized by following the same protocol as the synthesis of PFS_{26}-*b*-$PNIPAM_{520}$.[2] Other chemicals such as tetrahydrofuran (THF, purity ≥ 99.5%), methyl iodide (purity 99 %), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylenes (Karstedt's catalyst, 2 wt% Pt), 1,1,3,3-tetramethyldisiloxane (TMDS, purity ≥ 97%), and $HAuCl_4 \bullet 3H_2O$ (purity ≥ 99.999%) were purchased from Sigma-Aldrich.

1.2 Preparation of Quaternized PFS_{35}-b-$P2VP_{400}$ (PFS_{35}-b-$P2VP_{400}^{Q}$)

PFS_{35}-*b*-$P2VP_{400}^{Q}$ was synthesized through the reaction between PFS_{35}-*b*-$P2VP_{400}$ and methyl iodide.[3] PFS_{35}-*b*-$P2VP_{400}$ solid (10 mg) was dissolved in 1.0 mL of THF. Then methyl iodide (4.9 μL) was added. After gently shaking for 1 hour at room temperature (23 °C), the PFS_{35}-*b*-$P2VP_{400}^{Q}$

was obtained by precipitating in hexane. The degree of quaternization was determined to be 1 % by NMR in deuterated dimethyl sulfoxide (Figure S9).

1.3 Preparation of Seed Micelles

PFS_{35}-*b*-$P2VP_{400}$ seed micelles were prepared in two steps. First, long micelles (length > 5 μm, Figure S1a) were prepared by adding the BCP powder (1.0 mg) in iPrOH (1.0 mL), and heating the solution at 80 °C for 60 min, then slowly cooling to room temperature and aging for 24 h. Afterward, the suspension of long micelles was sonicated at room temperature for 30 min in a 70 W ultrasonic bath. The micelle seed fragments obtained (Figure S1b-c) were characterized by measuring over 200 seeds in several TEM images, using the software ImageJ.

1.4 Preparation of Patchy Micelles

Kinetics of single-component micelle growth. Before preparing samples of patchy micelles, we examined the growth rate of single-component micelles (homo-micelles) formed by seeded-growth of a single kind of unimer (PFS_{35}-*b*-$P2VP_{400}$, or PFS_{35}-*b*-$P2VP_{400}^{Q}$, or PFS_{26}-*b*-$PNIPAM_{190}$, or PFS_{26}-*b*-$PNIPAM_{520}$). In these experiments, a seed solution (20 μL, PFS_{35}-*b*-$P2VP_{400}$ seed micelles in iPrOH) was added to 0.98 mL of iPrOH. Individual unimer samples were dissolved in THF at a concentration of 10 mg/mL. Equimolar amounts of each unimer were injected to the diluted seed solution. For PFS_{35}-*b*-$P2VP_{400}$ unimer and PFS_{35}-*b*-$P2VP_{400}^{Q}$ unimer, 18 μL of the unimer THF solution was added; For PFS_{26}-*b*-$PNIPAM_{190}$, 10 μL unimer was added; For PFS_{26}-*b*-$PNIPAM_{520}$, 23 μL unimer was added. Aliquots of each micelle solution were taken at different times, transferred to a TEM grid and analyzed by TEM to monitor the increasing length of the micelles.

Patchy micelles. Patchy micelles were prepared in a similar way. Typically, a seed solution (5 μL, PFS_{35}-*b*-$P2VP_{400}$) was added to iPrOH (1.0 mL). In parallel, two unimer samples dissolved in THF were premixed in different ratios. Then 20 μL of the unimer mixture was injected into the seed solution and swirled for 10 s. The solutions were allowed to age for at least 3 days before TEM measurements.

1.5 In-situ Loading Metal Nanoparticles

Gold nanoparticles (AuNPs) were generated *in situ* after loading onto the patchy micelles. Typically, 100 μL of the micelle solution (ca. 0.1 mg/mL) was mixed with 10 μL $HAuCl_4 \cdot 3H_2O$ in iPrOH (1.0 mg/mL). The mixture was gently shaken for 1 hour; then the micelles were washed with iPrOH (3 times) to remove the free metal ions and then redispersed in iPrOH. An aliquot of the micelle solution was taken for TEM analysis. The AuNPs in situ formed by treating the micelle solution with $NaBH_4$.

Platinum nanoparticles (PtNPs) were selectively loaded into the P2VP domains of the patchy micelles. We have used this protocol in the past to crosslink P2VP corona chains in rod-like micelles and planar structures.[4,5] Typically, 25 μL of the patchy micelle solution was diluted to 100 μL in iPrOH. In 0.5 mL of iPrOH, 1 μL of Karstedt's catalyst and 1 μL of TMDS were mixed, and 10 μL of the mixture was added immediately to the micelle solution. The solution was shaken for a few seconds and then allowed to age for 1 day. In this way, PtNPs were formed and selectively loaded into the P2VP domains and the P2VP chains were also cross-linked by the PtNPs.

1.6 Electron microscopy characterization

TEM measurements were performed on a Hitachi HT7700 TEM operating at an accelerating voltage of 80 kV. Images were analyzed using ImageJ, an image processing program developed at the National Institutes of Health. A minimum of 200 individual micelles from several images were carefully measured to determine the contour length. The number-average length L_n and the weight-average length L_w of the micelles was calculated with the expressions (L = length of micelle, N = number)

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \tag{S1}$$

$$L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i} \tag{S2}$$

2. CALCULATION OF THE N_{agg} OF THE PATCHY MICELLES

The weight average length increment ($L_{final,w}$) of the comicelles after seeded-growth can be calculated by the following equation:

$$L_{final,w} = \frac{N_{unimer}}{N_{seed} N_{agg,L}} \tag{S3}$$

where N_{unimer} is the number of unimer chains added to the seeds solution, N_{seed} is the number of seeds at the initial state, $N_{agg,L}$ is the linear aggregation number of the BCP in the newly added block of the comicelles. Here, the weight average length increment is employed, as the $N_{agg,\,L}$ is a parameter related to the weight average molecular weight of the micelles ($M_{micelle,w}$) and the weight average micelle length ($L_{micelle,\,w}$), which can be written as eq S4

$$N_{agg,L} = \frac{M_{micelle,w} / M_{unimer}}{L_{micelle,w}} \tag{S4}$$

where M_{unimer} is the molecular weight of the unimer. This analysis assumes that the difference between $M_{w,\,unimer}$ and $M_{n,\,unimer}$ is very small.

N_{seed} can be obtained by eq S5

$$N_{seed} = \frac{m_{seed} N_A}{M_{0,seed} N_{agg,L,seed} L_{seed,w}} \tag{S5}$$

where m_{seed} is the mass of the seeds in the initial solution, $M_{0,seed}$ is the molecular weight of PFS_{35}-*b*-$P2VP_{400}$, $N_{agg,L,seed}$ is the linear aggregation number of BCP in the seeds (here $N_{agg,L,seed}$ = 2 molecules/nm, measured by laser light scattering),[1] $L_{seed,\,w}$ is the weight average length of the seeds, N_A is the Avogadro number.

N_{unimer} can be obtained by eq S6

$$N_{unimer} = \frac{m_{unimer}}{M_{unimer}} N_A \tag{S6}$$

where m_{unimer} is the mass of the unimers added to the seed solution.

Thus, by the combination of eq S3-S6, $L_{final,\,w}$ can be written as eq S7

$$L_{\text{final,w}} = \frac{N_{\text{unimer}}}{N_{\text{seed}} N_{\text{agg,L,grow}}} = \frac{m_{\text{unimer}}}{m_{\text{seed}}} \frac{M_{0,\text{seed}}}{M_{\text{unimer}}} \frac{N_{\text{agg,L,seed}}}{N_{\text{agg,L}}} L_{\text{seed,w}} \quad \text{(S7)}$$

Therefore, the aggregation number of the growing block can be calculated by the following equation,

$$N_{\text{agg,L}} = \frac{m_{\text{unimer}}}{m_{\text{seed}}} \frac{M_{0,\text{seed}}}{M_{\text{unimer}}} \frac{L_{\text{seed,w}}}{L_{\text{final,w}}} N_{\text{agg,L,seed}} \quad \text{(S8)}$$

This expression presumes that $L_{\text{seed,w}}$ and $L_{\text{final,w}}$ are determined from the same micelles. However, in some cases, it is difficult to accurately measure the length of the original seed in the central part of each micelle. Since the length distribution of the homomicelles, block comicelles, and patchy comicelles are very narrow ($L_w/L_n \leq 1.03$), we believe that the length distribution of the growing block is also very narrow. As a result, we can assume $L_{\text{final,w}} \approx L_{\text{final,n}}$, where $L_{\text{final,n}}$ is the number average length increment of the comicelles, and $L_{\text{final,n}} = L_{\text{total,n}} - L_{\text{seed,n}}$, where $L_{\text{total,n}}$ is the number average total length of the comicelles aged for at least 80 days. As the length distribution of the seeds is somewhat broader ($L_w/L_n = 1.11$), we apply $L_{\text{seed,w}}$ in eq S8 to calculate $N_{\text{agg,L,}}$. Therefore, eq S8 can be written as following

$$N_{\text{agg,L}} = \frac{m_{\text{unimer}}}{m_{\text{seed}}} \frac{M_{0,\text{seed}}}{M_{\text{unimer}}} \frac{L_{\text{seed,w}}}{L_{\text{final,n}}} N_{\text{agg,L,seed}} \quad \text{(S9)}$$

For patchy comicelles,

$$N_{\text{agg,L}} = \left(\frac{m_{\text{unimer1}}}{M_{\text{unimer1}}} + \frac{m_{\text{unimer2}}}{M_{\text{unimer2}}}\right) \frac{M_{0,\text{seed}}}{m_{\text{seed}}} \frac{L_{\text{seed,w}}}{L_{\text{final,n}}} N_{\text{agg,L,seed}} \quad \text{(S10)}$$

3. SUPPORTING FIGURES

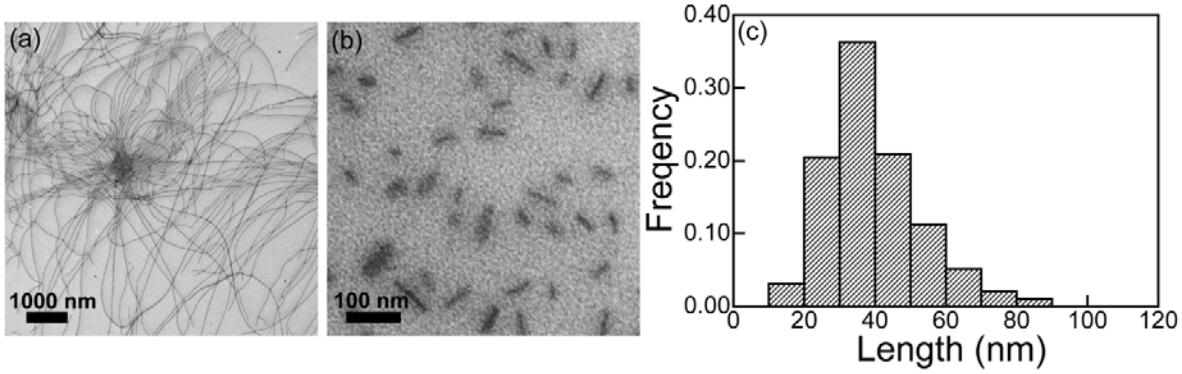

Figure S1. (a) Long micelles of PFS_{35}-*b*-$P2VP_{400}$ obtained by heating the BCP in iPrOH at 80 °C for 60 min, then slowly cooling to room temperature and aging for 24 h. (b) Micelle fragments of PFS_{35}-*b*-$P2VP_{400}$ obtained by ultrasonicating the long micelles shown in (a) for 30 min at 23 °C. These short micelles were employed as seeds for directing the epitaxial growth of BCP unimers. (c) Histogram of the contour length of the seeds shown in (b). L_n = 40 ± 13 nm, L_w/ L_n = 1.11.

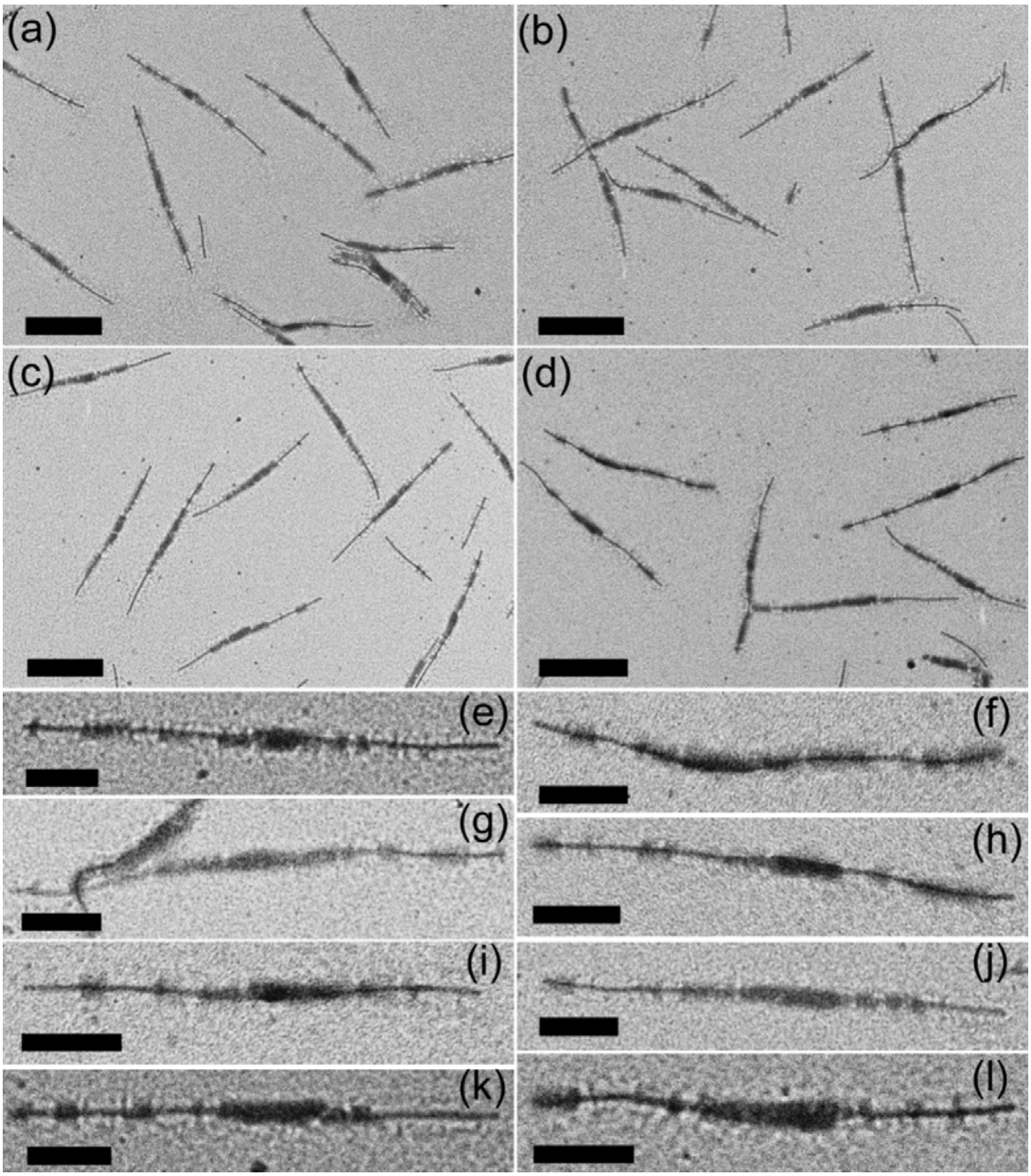

Figure S2. Additional TEM images of the patchy micelles shown in Figure 1a. The mass ratio of PFS_{35}-*b*-$P2VP_{400}$ to PFS_{26}-*b*-$PNIPAM_{190}$ is 1:1. The scale bars in (a)-(d) are 500 nm and in (e)-(l) are 200 nm.

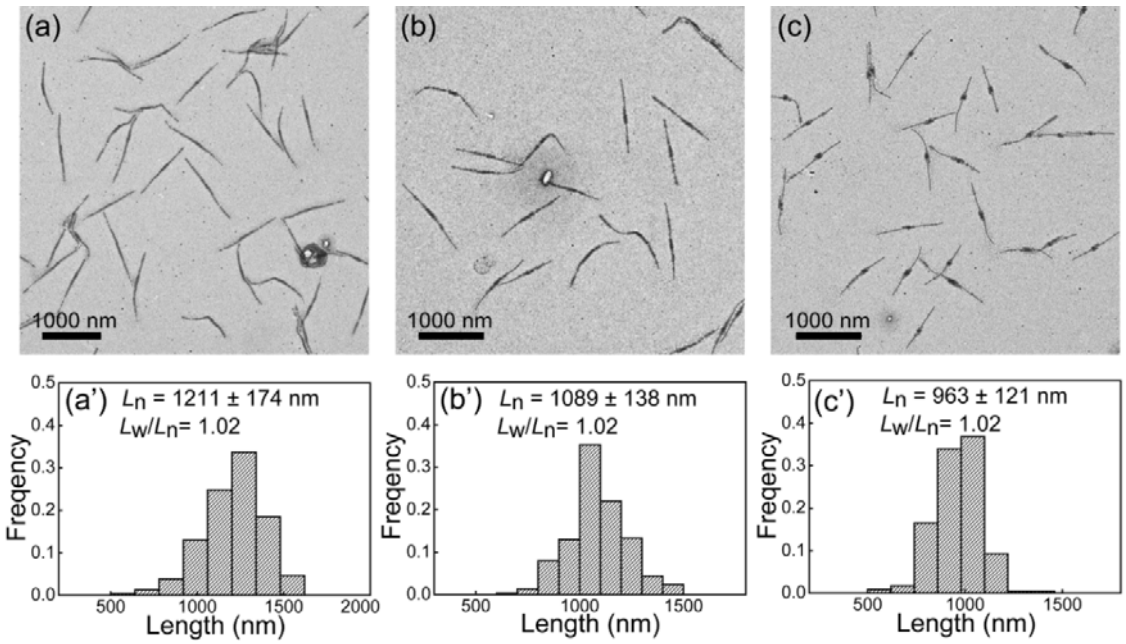

Figure S3. TEM images and the corresponding histograms of the contour length of the patchy micelles shown in Figure 1. The mass ratios of PFS_{35}-*b*-$P2VP_{400}$ to PFS_{26}-*b*-$PNIPAM_{190}$ are (a) and (a') 3:1, (b) and (b') 1:1, (c) and (c') 1:3, respectively. The unimer-mixture-to-seed weight ratio was 40:1.

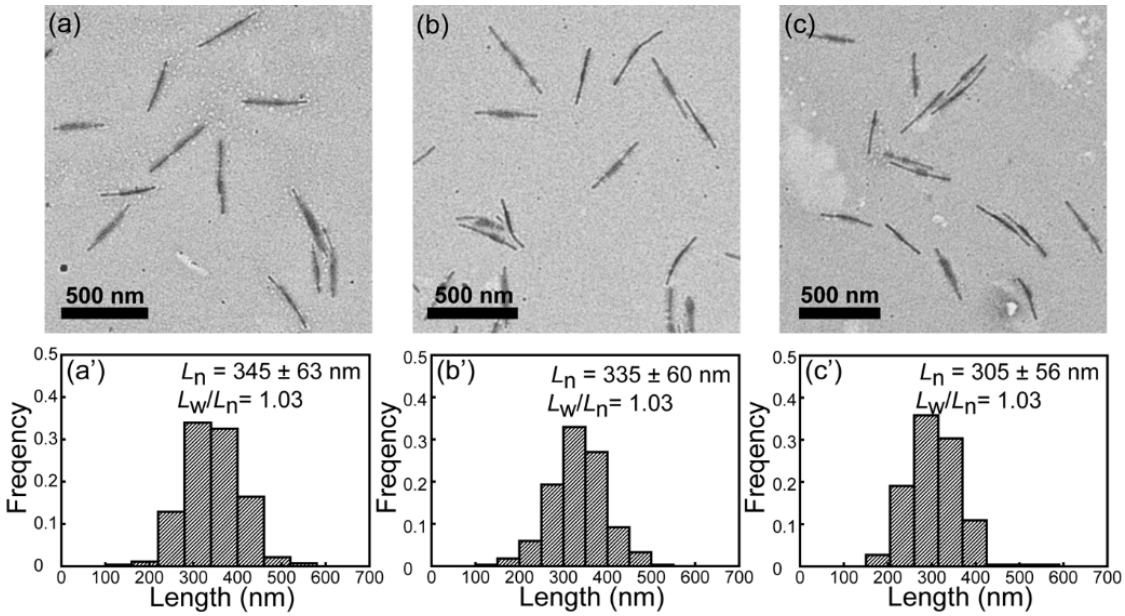

Figure S4. TEM images (a-c) and their corresponding histograms (a'-c') of the contour length of the micelles obtained by growing a mixture of PFS_{35}-*b*-$P2VP_{400}$/PFS_{26}-*b*-$PNIPAM_{190}$ unimers on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ Ln = 1.11). For each example, the total number of moles of BCP unimer added was the same. The molar ratios of PFS_{35}-*b*-$P2VP_{400}$ to PFS_{26}-*b*-$PNIPAM_{190}$ in the unimer mixtures are (a) 3:1, (b) 1:1, and (c) 1:3, respectively.

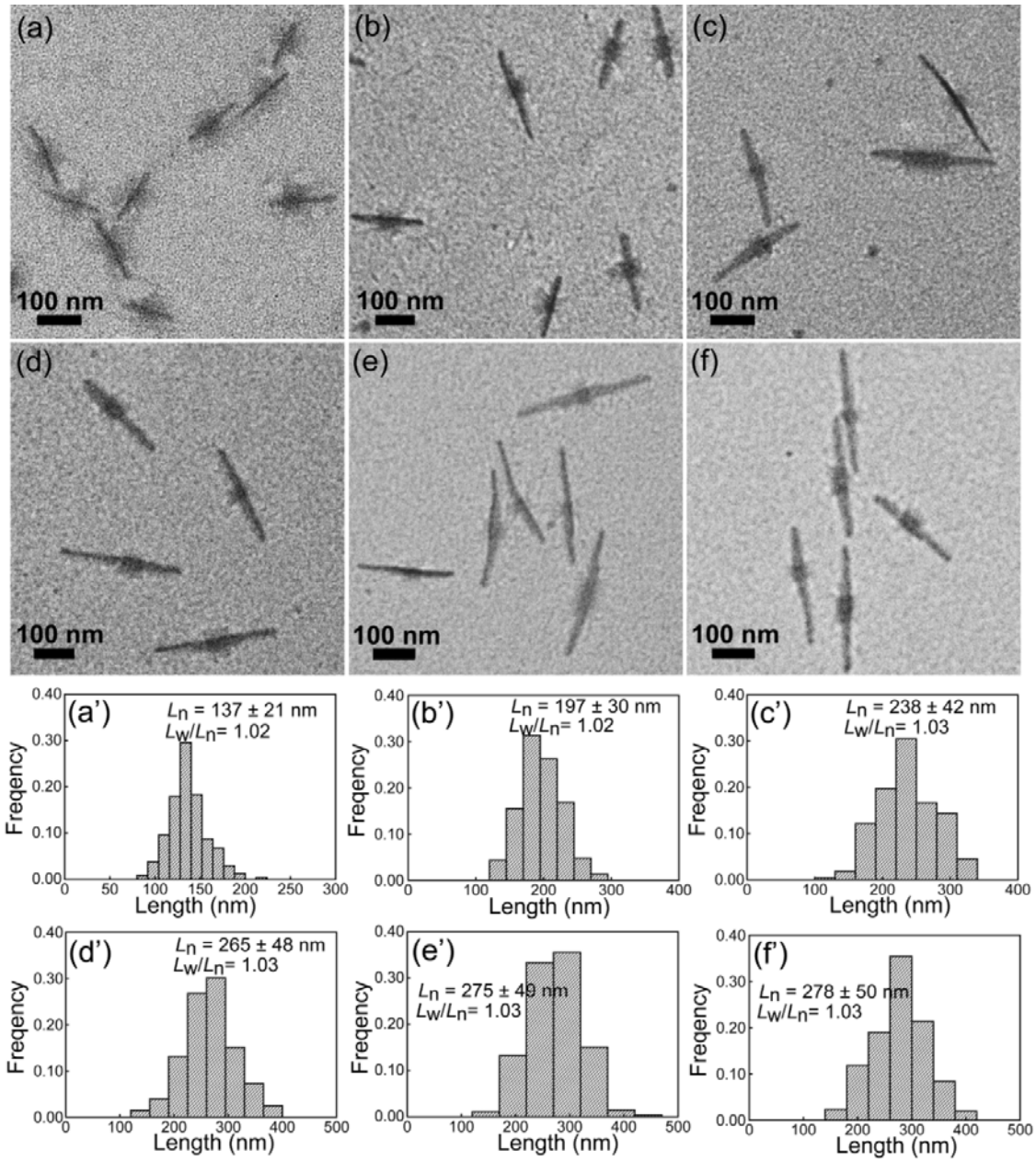

Figure S5. TEM images (a-f) and their corresponding histograms (a'-f') of the contour lengths of the micelles obtained by growing PFS_{26}-*b*-$PNIPAM_{190}$ unimer on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ L_n = 1.11). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1000 min, (d) and (d') 7 days, (e) and (e') 60 days, (f) and (f') 110 days, respectively.

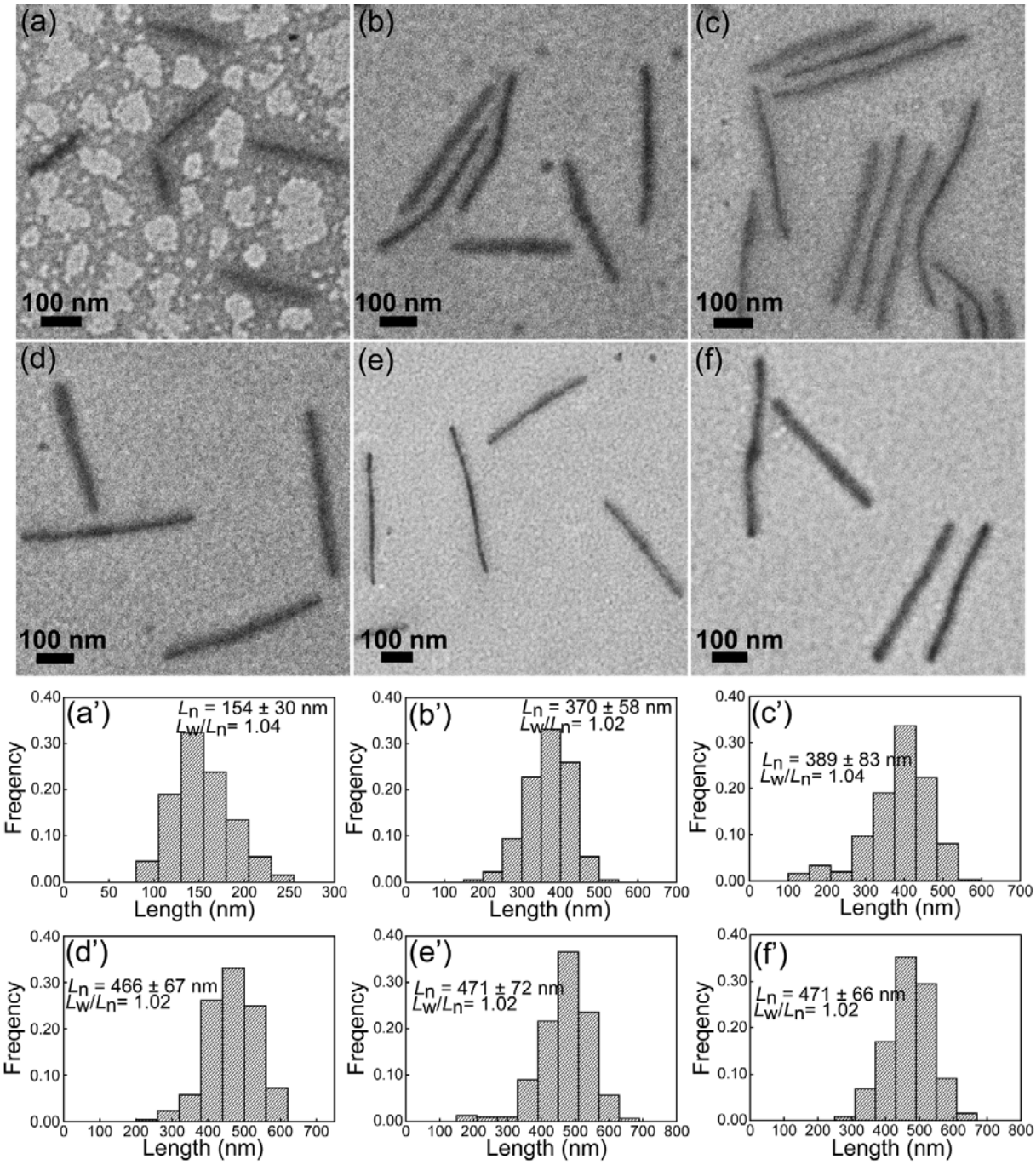

Figure S6. TEM images (a-f) and their corresponding histograms (a'-f') of the contour lengths of the micelles obtained by growing PFS_{35}-*b*-$P2VP_{400}$ unimer on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ L_n = 1.11). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1000 min, (d) and (d') 7 days, (e) and (e') 60 days, (f) and (f') 110 days, respectively.

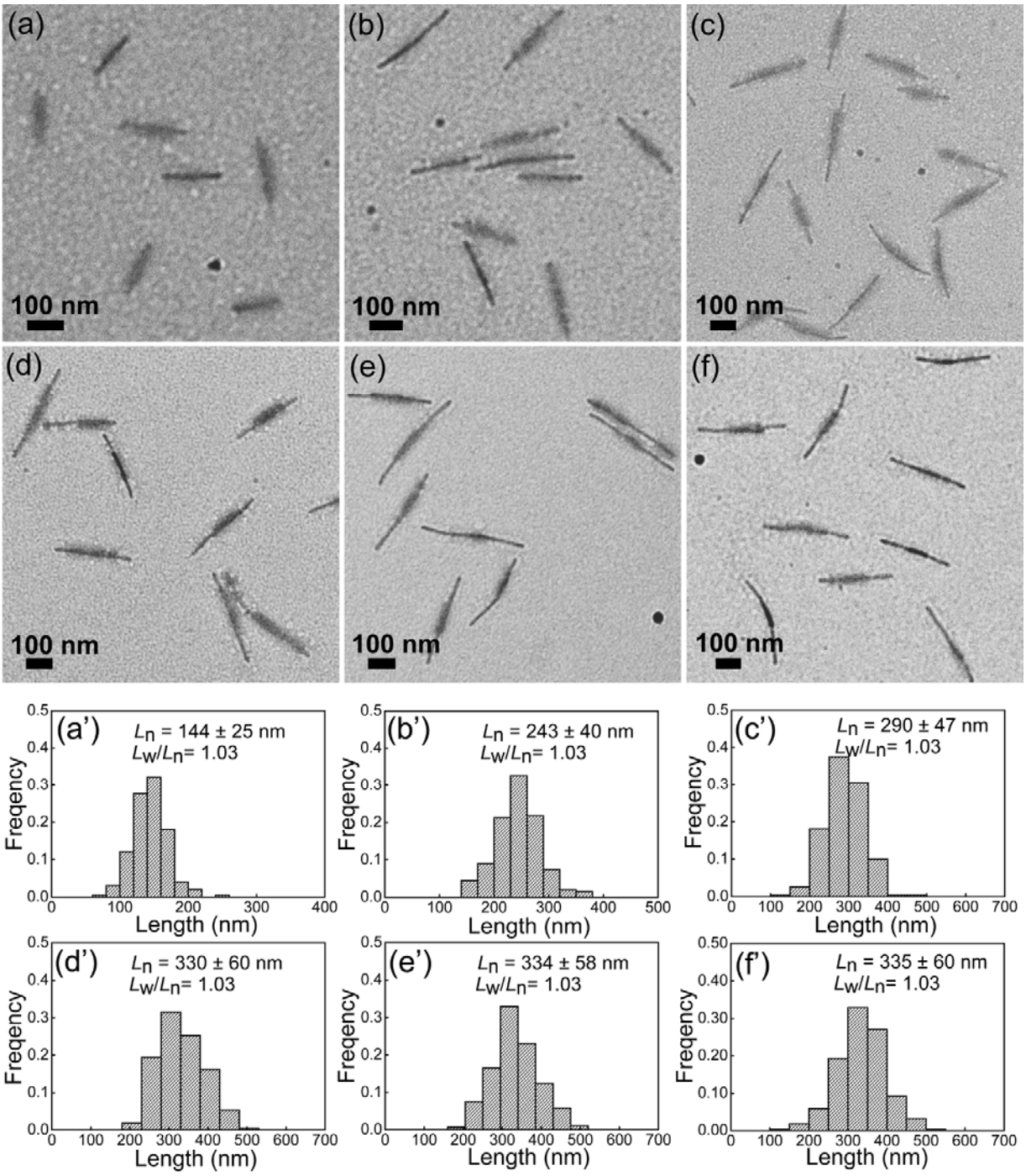

Figure S7. TEM images (a-f) and their corresponding histograms (a'-f') of the contour lengths of the micelles obtained by growing PFS_{35}-*b*-$P2VP_{400}$/PFS_{26}-*b*-$PNIPAM_{190}$ mixed unimers (molar ratio 1:1) on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ L_n = 1.11). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1000 min, (d) and (d') 7 days, (e) and (e') 35 days, (f) and (f') 80 days, respectively.

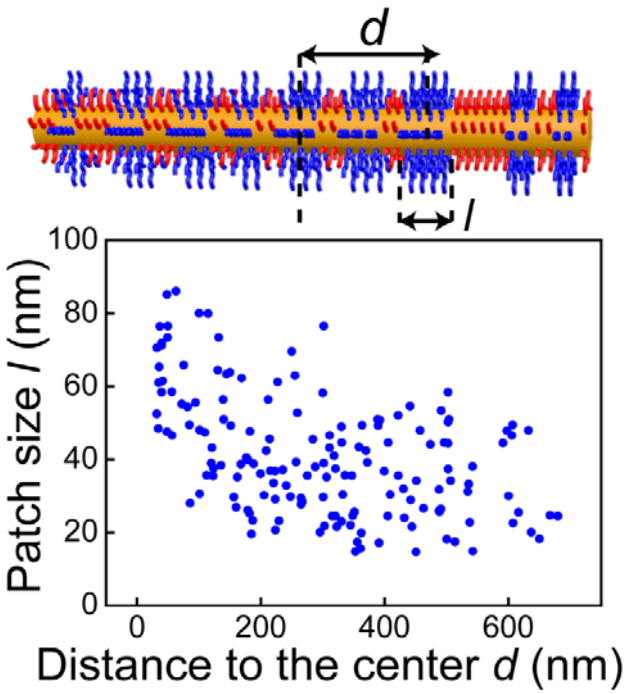

Figure S8. Plot shows the relationship between the PFS_{35}-*b*-$P2VP_{400}$ patch size (*l*) and its distance (*d*) to the central part (seed) of the patchy micelles. These data were obtained by measuring the PFS_{35}-*b*-$P2VP_{400}$ patch length and the patch-to-seed distance from 21 patchy micelles (molar ratio of PFS_{35}-*b*-$P2VP_{400}$ to PFS_{26}-*b*-$PNIPAM_{190}$ was 1:1). The result indicates that the size of PFS_{35}-*b*-$P2VP_{400}$ patch decreased as when it was further away from the center of the micelle.

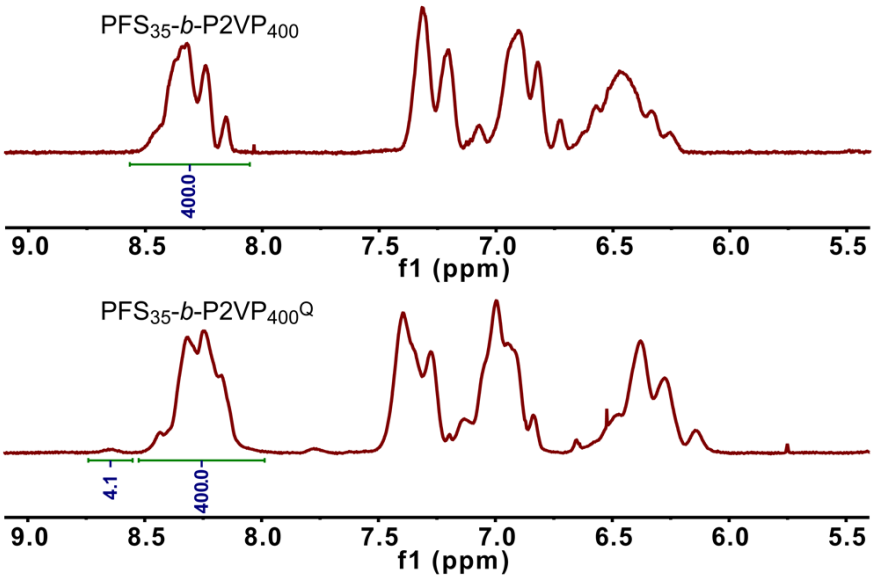

Figure S9. ^{1}H NMR spectra of PFS_{35}-*b*-$P2VP_{400}$ (upper spectrum) and PFS_{35}-*b*-$P2VP_{400}^{Q}$ (bottom spectrum) in deuterated dimethyl sulfoxide. The degree of quaternization of the BCPs was evaluated to be 1 % (4.1/(400+4.1)) by ^{1}H NMR by comparing the integration of the α-proton signal of the pyridinium units at 8.7 ppm to the α-proton signal of the pyridine units at 8.3 ppm.

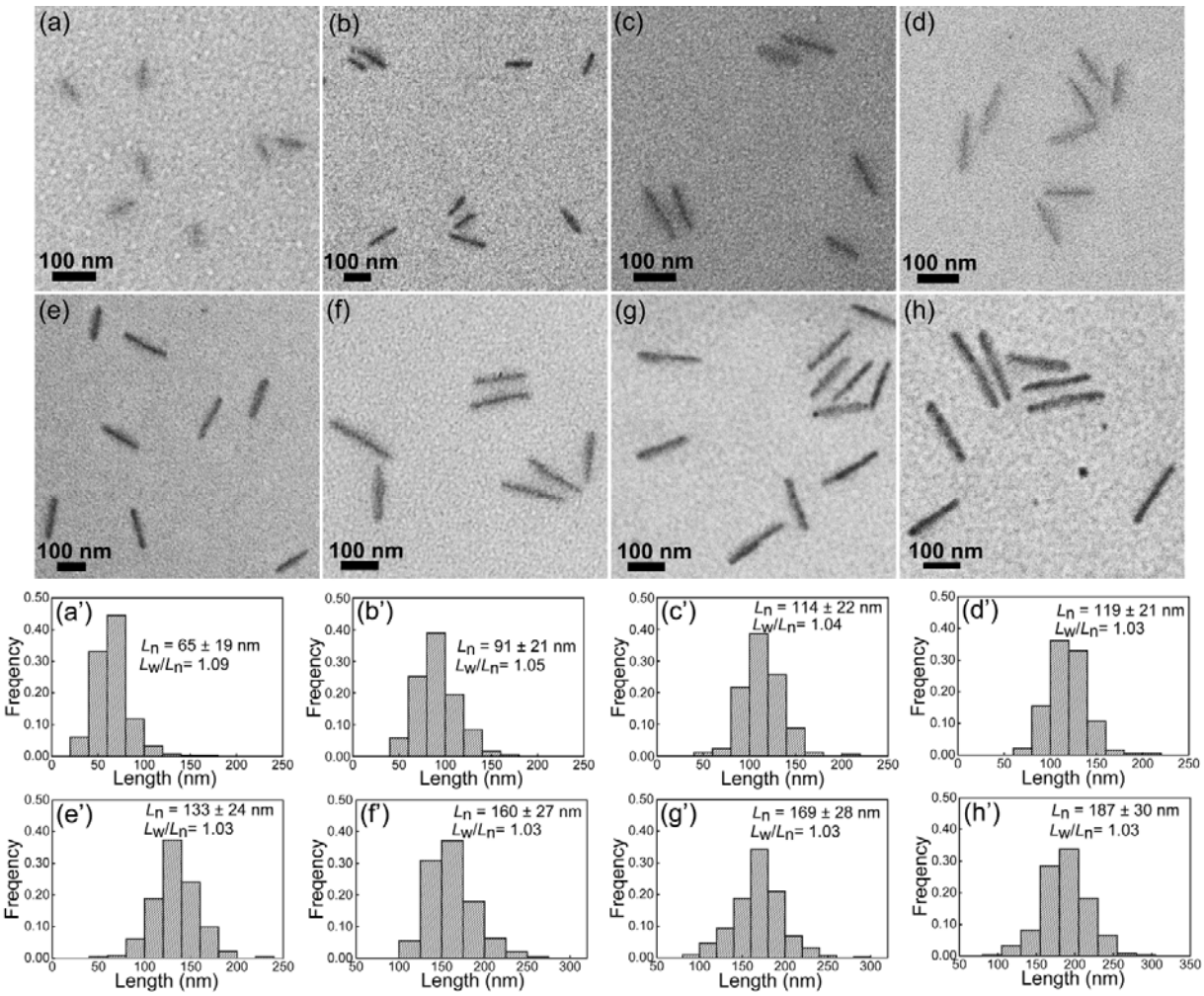

Figure S10. TEM images (a-h) and their corresponding histograms (a'-h') of the contour lengths of the micelles obtained by growing PFS_{35}-*b*-$P2VP_{400}^{Q}$ unimer on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ L_n = 1.11). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1000 min, (d) and (d') 3000 min, (e) and (e') 7 days, (f) and (f') 30 days, (g) and (g') 60 days, (h) and (h') 110 days, respectively.

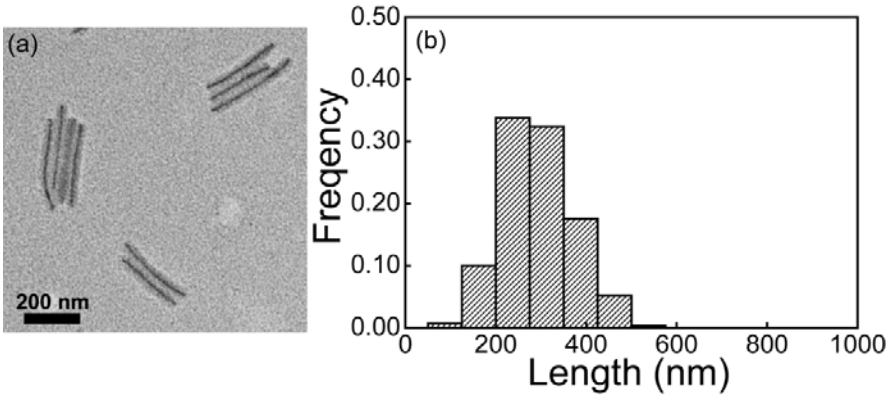

Figure S11. (a) PFS_{26}-*b*-$PNIPAM_{190}$ seed micelles. (b) Histogram of the contour length of the seeds. L_n = 290 ± 76 nm, L_w/L_n = 1.07.

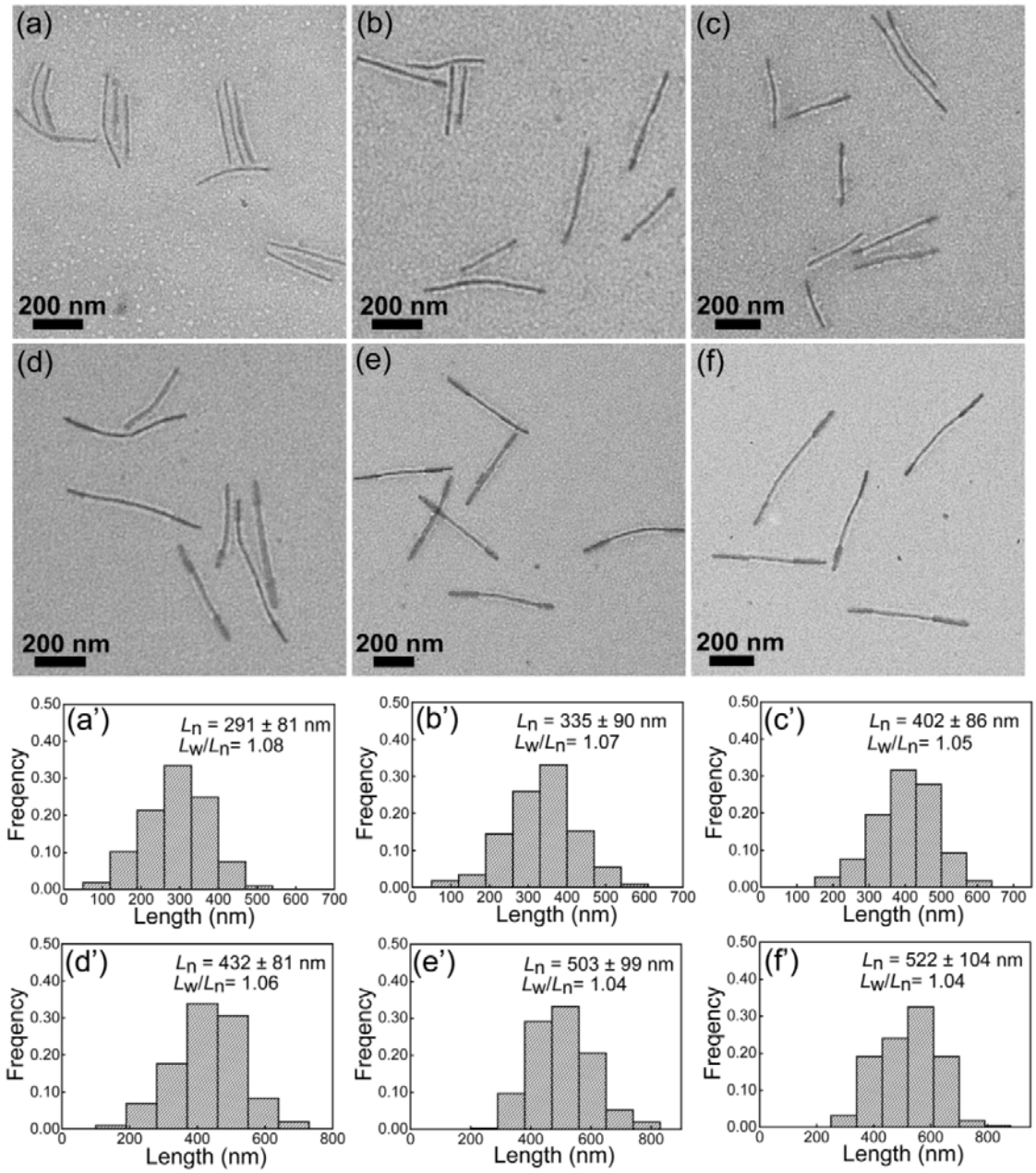

Figure S12. TEM images (a-f) and their corresponding histograms (a'-h') of the contour lengths of the micelles obtained by growing PFS_{35}-*b*-$P2VP_{400}^{Q}$ unimer on PFS_{26}-*b*-$PNIPAM_{190}$ seed micelles (L_n = 290 ± 76 nm, L_w/ Ln = 1.07). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1000 min, (d) and (d') 7 days, (e) and (e') 45 days, (f) and (f') 80 days, respectively.

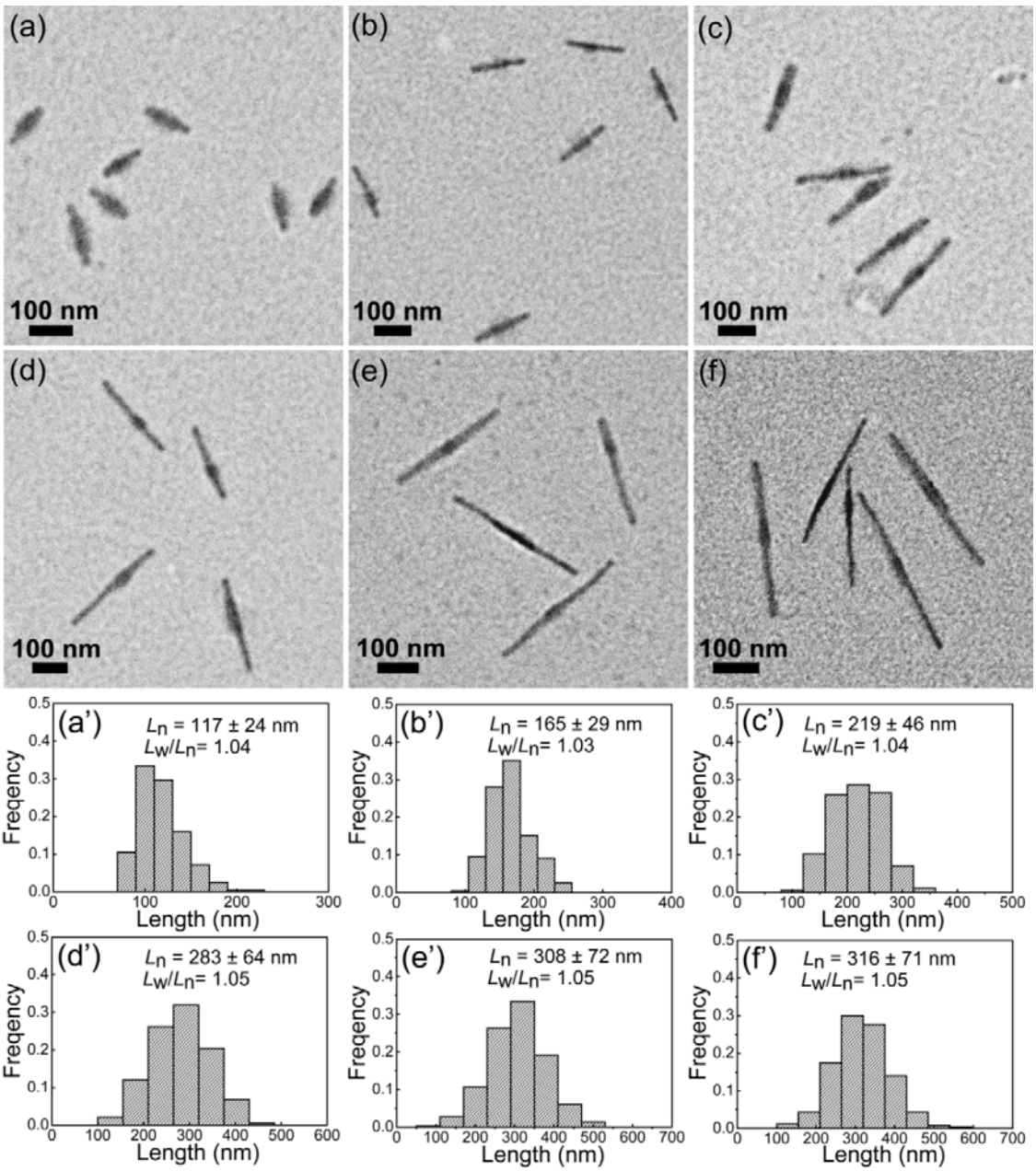

Figure S13. TEM images (a-h) and their corresponding histograms (a'-h') of the contour lengths of the micelles obtained by growing PFS_{26}-*b*-$PNIPAM_{520}$ unimer on PFS_{35}-*b*-$P2VP_{400}$ seeds (L_n = 40 ± 13 nm, L_w/ L_n = 1.11). The aging times were (a) and (a') 10 min, (b) and (b') 100 min, (c) and (c') 1115 min, (d) and (d') 8 days, (e) and (e') 35 days, (f) and (f') 80 days, respectively.

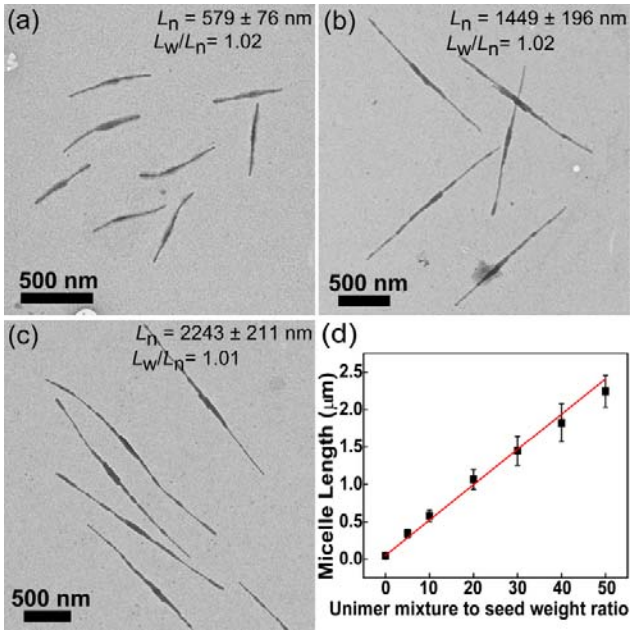

Figure S14. Controlling the length of the patchy cylindrical micelles by varying the weight ratio of unimer mixture (PFS_{26}-b-$PNIPAM_{190}$/PFS_{35}-b-$P2VP_{400}$, weight ratio 1:1) to seed. (a)-(c) are the TEM images of the patchy micelles in which the weight ratios of unimer mixture to seed are 10:1, 30:1, and 50:1, respectively. (d) shows that the length of the patchy micelles increased linearly as the weight ratio of unimer mixture to seed.

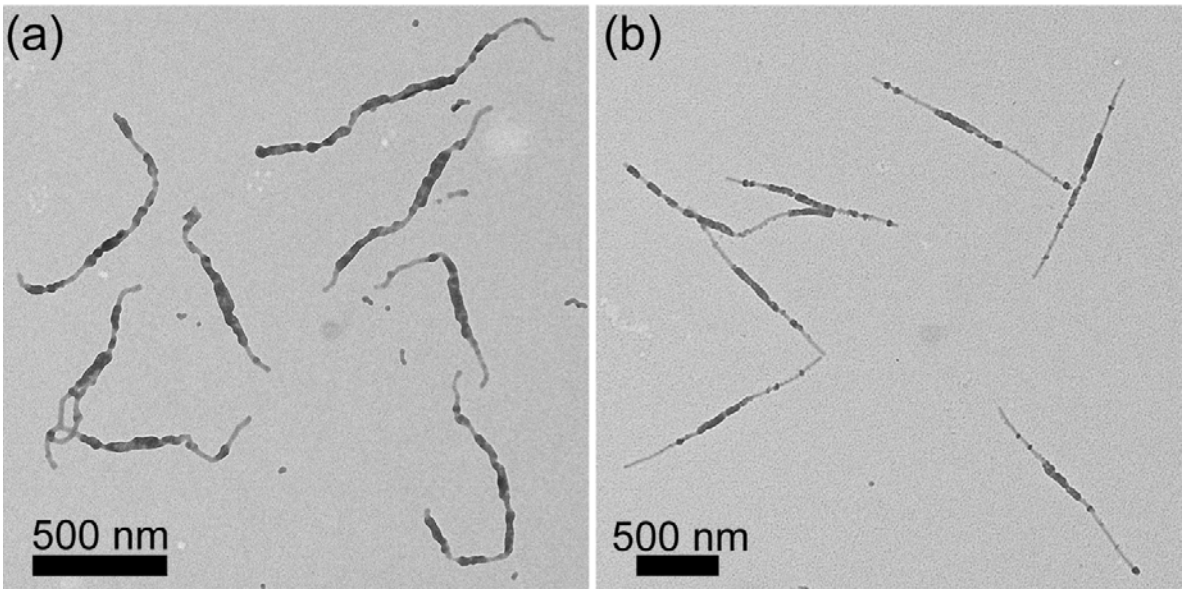

Figure S15. Additional TEM images of the patchy comicelles loaded with (a) AuNPs and (b) PtNPs. These hybrid structures were prepared using the patchy micelles shown in Figure 1a,d, in which a 1:1 (w/w) mixture of PFS_{35}-*b*-$P2VP_{400}$ and PFS_{26}-*b*-$PNIPAM_{190}$ were added to PFS_{35}-*b*-$P2VP_{400}$ seed micelles. It is interesting to note that the hybrid micelles in (a) are bent, suggesting that they are flexible, while those in (b) are rigid. This difference may be due to the interaction between PFS and $HAuCl_4$. PFS is sensitive to acid, and there may be some decomposition of the PFS block caused by the acidity of $HAuCl_4$.

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