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SUPPORTING INFORMATION

Monitoring collapse of uniform thermoresponsive cylindrical brushes in water

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EXPERIMENTAL SECTION

1. Instrumentation

Gel Permeation Chromatography (GPC) measurements were carried out with a Waters 515 HPLC equipped with a Viscotek VE 3580 RI detector, and a 2500 UV-Vis detector in conjunction with poly(methyl methacrylate) standards. THF containing 0.25 g/L tetra-*n*-butylammonium bromide (TBAB) was used as the eluent (flow rate = 0.6 mL/min).

¹H NMR (500 MHz) spectra were recorded on an Agilent 500 spectrometer with a 45° pulse angle and 10 s delay time at 25 °C. Solution turbidity was measured at 500 nm using a Perkin Elmer Lambda 35 UV/Vis spectrometer.

MALDI-TOF measurements were carried out on an Applied Biosystems 4700 Proteomics analyzer in the reflector mode. A dithranol matrix (20mg/mL, THF) was used with the polymer sample (10 mg/mL, THF) in a 1:10 (v/v) ratio. About 1 µL of the mixed solution was deposited on the sample plate and allowed to dry before data acquisition.

Transmission electron microscopy (TEM) measurements were performed on a Hitachi D-7000 microscope or a Hitachi HT7700 microscope operating at an accelerating voltage of 100 kV in the bright-field TEM mode. Samples were prepared by placing a drop of solution on a Formvar-coated TEM grid and removing excess liquid with the edge of a filter paper. Images were analyzed with the software Image J (NIH, USA). A minimum of 100 individual fiber-like micelles were carefully traced by hand to determine the contour length. From this data L_n and L_w

of each sample of cylindrical micelles was calculated as shown below (L_i = length of object i , N_i = number of objects of length i).

$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} \quad L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \quad (S1)$$

Static (SLS) and dynamic light scattering (DLS) measurements were performed using a wide angle light scattering photometer from ALV. The light source was a JDS Uniphase He-Ne laser ($\lambda = 632.8$ nm, 35 mW) emitting vertically polarized light. The cells were placed into the ALV/DLS/SLS-5000 Compact Goniometer System and sat in a vat of toluene, which matched the index of refraction of the glass cells. The scattered light was detected by a Dual ALV-High Q.E. APD avalanche photodiode module, interfaced to the ALV-5000/EPP multiple tau digital. Most measurements were carried out at 23.00 ± 0.05 °C. Some measurements were made for solutions at temperatures between 30 °C and 50 °C as described below. Data were collected for 90 s at each scattering angle. The angular range consisted of scattering angles between 20° and 60° at 2° intervals, between 63° and 90° at 3° intervals, and at angles between 95° and 150° at 5° intervals. SLS and DLS measurements were carried out simultaneously. Toluene was used as the standard in the SLS measurements.

2. Materials and Methods

All chemicals were purchased from Sigma-Aldrich. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) ($M_n = 500$) and di(ethylene glycol)methyl ether methacrylate (MEO₂MA) were purified by passing them through an inhibitor removal column. All the other chemicals and solvents were used as received. The syntheses of alkyne-terminated polyferrocenylsilane (PFS₂₆-≡, $DP = 26$) was described in a previous publication.¹ The polymer was characterized by MALDI-TOF as shown in Figure S1, with m/z peaks found at $243.0n + 260$. (The molecular weight of PFS repeat unit is 243.0 Da; the sum of *n*-butyl and the TMS-aryl-alkyne end groups is 260 Da). $M_n^{\text{MALDI}} = 6.8$ kDa, $\bar{D} = 1.03$, GPC (THF/TBAB, RI): $M_n^{\text{GPC}} = 6.0$ kDa, $\bar{D} = 1.05$

Azide-functionalized Copolymerization of MEO₂MA and OEGMA (POEGMA). In a typical ATRP synthesis of POEGMA (see Scheme S1), OEGMA (0.7 g, 1.4 mmol), MEO₂MA

(2.4 g, 12.6 mmol) CuBr (20 mg, 0.14 mmol), and 2,2'-bipyridyl (42.7 mg, 0.28 mmol) were dissolved in methanol (6 mL) in a 25 mL Schlenk tube. After three cycles of freeze-pump-thaw, the azide-functionalized initiator 2-azidoethyl 2-bromoisobutyrate (33 mg, 0.14 mmol) was introduced by a micro syringe to start the polymerization at 60 °C. The reaction was run overnight and terminated by exposure to air and dilution with THF. An aliquot was removed for monomer conversion determination by NMR. Then the solution was precipitated by injecting into 50 mL of diethyl ether under vigorous stirring followed by re-dissolving in THF and passing through an aluminum oxide column to remove the copper catalyst. Another two cycles of dissolution in THF and precipitation in ether gave samples of POEGMA-N₃ that were then dried in a vacuum oven overnight. The polymer was subjected to GPC analysis. Monomer conversion: 75%. ¹H NMR (CDCl₃, 500 MHz, Figure S2): δ (ppm) = 0.80-2.15 (broad, 5H, polymer backbone, integration = 5.1), 3.41 (s, 3H, O-CH₃, integration = 3.0), 3.51-3.72 (m, 34H for OEGMA and 6H for MEO₂MA, O-CH₂-CH₂-O, integration = 8.80), 4.10 (s, 2H, COOCH₂, integration = 1.97), GPC (THF/TBAB, RI): M_n^{GPC} = 25.0 kD, Đ = 1.30. End-group determination by ¹H-NMR was not possible due to signal overlap of initiator and polymer protons.

Scheme S1. Synthesis of PFS₂₆-*b*-POEGMA₁₆₃ by a Combination of ATRP and Copper-Catalyzed Azide-Alkyne Coupling

Synthesis of PFS₂₆-*b*-POEGMA₁₆₃. The diblock copolymer PFS₂₆-*b*-POEGMA₁₆₃ was prepared via Cu-catalyzed alkyne azide cycloaddition (CuAAC) reaction between alkyne-terminated PFS₂₆-≡ and POEGMA₁₆₃-N₃ (Scheme S1). PFS₂₆-≡ (30 mg, 4.3 μmol), POEGMA-N₃ (180 mg), and PMDETA (9 μL, 0.043 mmol) were dissolved in THF (3 mL) in a Schlenk tube. After three cycles of freeze-pump-thaw, the Schlenk tube was transferred to a N₂-protected

glovebox followed by addition of CuCl (4.3 mg, 0.043 mmol). Then the reaction was allowed to stir at 40 °C for 4 days before being quenched by exposure to air. Aliquots of the mixture were removed before and after the reaction to monitor the reaction progress by GPC. The solution was then diluted with THF and passed through an Al₂O₃ column to remove the copper catalyst.

As indicated in the GPC curves after reaction (Figure S3), the block copolymers contained small amounts of unreacted PFS and POEGMA homopolymer. To purify the diblock copolymer, the crude product was first centrifuged at 15000 g in THF to remove any undissolved residues followed by slow addition of n-hexane until a brown precipitate was observed. Centrifugation to isolate the sediment and repeat of the process removed most of the residual PFS homopolymer. Then the sediment was redissolved in small amount of THF (ca. 1 mL), and ethanol (5 mL) was added. The solution was heated at 60 °C for 30 min, then aged at room temperature overnight. Under these conditions, the diblock copolymer forms large aggregates. Centrifugation to isolate the aggregates followed by washing two times with ethanol eliminated most of the POEGMA homopolymer. After drying, we obtained the diblock copolymer (60 mg, yield 40%). The polymer was analyzed by GPC and by NMR.

The coupling reaction was monitored by GPC with both RI and UV-Vis detectors over the reaction time. From the GPC curves (Figure S3), clear peak shifts could be identified from both signals, indicating the successful coupling of two polymers. We also infer a 5% residual impurity of PFS homopolymer in the BCP sample after purification. To calculate the degree of polymerization (DP) of POEGMA, we first determined the block ratio of PFS to POEGMA by analyzing ¹H-NMR peak integrations of the purified di-block copolymer in CD₂Cl₂ as shown in Figure S4. By comparing the integration of peaks from the Cp rings on PFS and the methylene groups on POEGMA, we calculate a block ratio of 6.3 (accounting for ~5% remaining PFS homopolymer). Using the PFS signal (*DP* = 26) as a reference, we calculated *DP* = 163 for POEGMA. Thus the diblock copolymer is denoted as PFS₂₆-*b*-POEGMA₁₆₃.

¹H NMR (CD₂Cl₂, 500 MHz, Figure S4): δ (ppm, integrated peak areas reported are based on Cp protons (4H, Cp) as the reference) = 0.48 (s, 6H, -Si(CH₃)₂-Cp, integration = 6.01), 0.80-1.95 (broad, 5H, polymer backbone), 3.35 (s, 3H, O-CH₃, integration = 17.74), 3.51-3.72 (m, 34H for OEGMA and 6H for MEO₂MA, O-CH₂-CH₂-O, integration = 52.03), 4.01 (s, 4H, Cp, integration = 3.96), 4.06-4.12 (broad, 2H, COOCH₂, integration = 12), 4.22 (s, 4H, Cp, integration = 4.00),. GPC (THF/TBAB, RI): *M_n*^{GPC} = 31.6 kDa, Đ = 1.28. .

3. Micelle formation

We used two different approaches in an attempt to prepare long fiber-like micelles of PFS₂₆-*b*-POEGMA₁₆₃. In the direct assembly (DA) approach, samples of the block copolymer (BCP) and solvent were mixed at a concentration of 0.2 mg/mL in a 7-mL vial. The sealed vials were placed in a heating block at 80 °C for 1 h, followed by slow cooling in which the block was left to cool to room temperature (RT). Subsequently, the solutions were allowed to age for several days. In the solvent-assisted approach, the block polymer was first dissolved in THF (20 mg/mL) and then 10 µL was injected into 1 mL of solvent pre-heated to 80 °C giving a final BCP concentration of 0.2 mg/mL. These solutions were allowed to cool slowly in the heating block and then were aged for several days. The results for each solution are summarized in Table S2. Figure S5 shows TEM images of the structures obtained using these different approaches.

Seeded growth experiments. Preliminary seeded growth experiments were carried out on the mixture of spheres and short rods from direct assembly (DA) formed in methanol and formed in the methanol/ethanol mixture. Both samples were subjected to mild sonication (70 watt ultrasonic cleaning bath, 30 min at 23 °C) to prepare seed solutions. These seed solutions were then diluted with the same solvent 20× to 10 µg/mL, and 2 mL solution were transferred to new vials for seeded growth experiments. Aliquots (2 µL, 5 µL and 10 µL) of PFS₂₆-*b*-POEGMA₁₆₃ in THF (20 mg/mL), referred to as “unimer” solutions, were added into each seed solution and swirled for 10 s. Each solution was allowed to age in the dark for 7 days. TEM images of the structures formed in methanol are shown in Figure S6.

We then carried out similar experiments with seed fragments formed from the long micelles prepared by THF-assisted (TA) self-assembly in the methanol/ethanol (1:4, v/v) mixture. After an aliquot was taken for TEM analysis (c.f., Figure 1A, main text), the seed solution was diluted with the same solvent 20× to 10 µg/mL. As in the preceding experiments, aliquots (2 µL, 5 µL and 10 µL) of PFS₂₆-*b*-POEGMA₁₆₃ in THF (20 mg/mL) were added into each seed solution and swirled for 10 s. Each solution was allowed to age in the dark for at least 7 days before TEM measurements. In these experiments in which there was no background of spherical entities accompanying the seed fragment, we obtained rod-like micelles of uniform length (c.f, Figure 1, main text). For these experiments, we took special care to ensure that all of the added unimer had deposited onto micelles after aging for 7 days. Here the longest micelle

samples were re-characterized by TEM after aging for 30 days. No noticeable length changes were noticed. A summary of all the structures formed are collected in Table S3.

Micelle transfer to water and to methanol. Solvent transfer experiments were carried out with rod-like micelle samples of uniform length prepared by seeded growth in methanol/ethanol 1:4 v/v. Aliquots (40 μ L) of each micelle sample in the methanol/ethanol mixture were injected into 1 mL of methanol or water. We made no attempt to remove residual mother solvent. The micelles in these solutions were characterized by TEM and by light scattering. See Figure S7 for TEM images and histograms of the micelles after transfer to methanol and to water.

ADDITIONAL RESULTS AND DISCUSSION

Self-assembly experiments

We used two different approaches in an attempt to prepare long fiber-like micelles of PFS₂₆-*b*-POEGMA₁₆₃. In the direct assembly (DA) approach, samples of the BCP as a solid were added to methanol, ethanol, 2-propanol or a 1:4 v/v mixture of methanol and ethanol. The samples were heated to 80 °C and allowed to cool. Experiments with 2-propanol led only to a solid precipitate. TEM images of the objects obtained in this way from the other solvents are presented in the top row of Figure S5. They consist of mixtures of short rods and smaller spheres. In the THF-assisted (TA) self-assembly approach, a solution of the polymer in THF (10 μ L) was injected into 1 mL of solvent preheated to 80 °C and allowed to cool. TEM images of the structures formed are presented in the bottom row of Figure S5. The sample in methanol formed lenticular micelles. The sample in ethanol yielded a turbid solution that consisted of dense aggregates of fiber-like micelles. The sample in the methanol-ethanol mixture gave a transparent solution of long thin fiber-like micelles. Most experiments were carried out with this sample. A summary of the structures formed is collected in Table S2.

Seeded growth experiments were carried out on the DA sample prepared in methanol and on both samples prepared in the methanol-ethanol mixture following sonication to obtain shortened seed micelles. The results of experiments in methanol with the mixture of short rods and spheres obtained by the DA approach are shown in Figure S6. Here it appears that added unimer grew epitaxially off the ends of the short rods, but the spherical micelles remained unchanged. Similar results were obtained for the mixture of short rods and spherical micelles in the methanol-ethanol

mixture. These results support the idea that the spherical micelles are amorphous structures that cannot initiate CDSA.

Seeded growth experiments with the micelle fragments obtained by sonication of the long fiber-like micelles obtained by the TA approach (c.f., Figure S5F) are described extensively in the main text. One can calculate a “theoretical” micelle length $L_{\text{theoretical}}$ for these structures based on the assumptions that 1) all added unimer deposits onto the ends of seed micelles, 2) no nucleation to form new micelles, and 3) the number of polymer molecules per unit micelle length does not change during the growth.

$$L_{\text{theoretical}} = \left(\frac{m_{\text{unimer}}}{m_{\text{seed}}} + 1 \right) L_{\text{seed}} \quad (\text{S2})$$

Here L_{seed} describes the number-averaged length of the seeds, m_{unimer} is the mass of polymer in THF that was added to the seeds and m_{seed} is the mass of polymer in the seeds.

TEM images of uniform micelles after transfer to methanol and to water are presented in Figure S7. The lengths of all the micelles obtained by seeded growth before and after transfer to methanol and water are collected in Table S3.

Micelle characterization by light scattering

The rod-like micelles of uniform length prepared by seeded growth were examined by simultaneous SLS and DLS measurements. In multi-angle SLS measurements, we obtain structural and dimensional information by measuring the excess scattered intensity (Rayleigh ratio, R_θ). For rigid rods of length L and cross section radius R_{SLS} , R_θ is related to concentration c , and the form factor $P(q)$ as:

$$f(q) = \frac{q R_\theta}{\pi M_0 K c} = \frac{P(q) \cdot q}{\pi} \cdot L \cdot N_{\text{agg}} / L \quad (\text{S3})$$

where

$$P(q, L, R_{\text{SLS}}) = \int_0^{\frac{\pi}{2}} \left(\left[2 \left(\frac{\sin\left(\frac{qL \cos \alpha}{2}\right)}{\frac{qL \cos \alpha}{2}} \right) \right] \frac{J_1(q R_{\text{SLS}} \sin \alpha)}{q R_{\text{SLS}} \sin \alpha} \right)^2 \sin \alpha d\alpha \quad (\text{S4})$$

$K = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda_0^4)$, $q = (4\pi n / \lambda_0) / \sin(\theta/2)$, and N_A , n , λ_0 and θ are the Avogadro number, the solvent refractive index, the wavelength of the light in vacuum, and the scattering angle, respectively. For block copolymers, the specific refractive index increment $(dn/dc)_{\text{polymer}}$ is related to the dn/dc values of the components via the weight fractions w_j of monomer type j in the polymer (with $\sum_{j=1} w_j = 1$):

$$\left(\frac{dn}{dc}\right)_{polymer} = \sum_{j=1} w_j \left(\frac{dn}{dc}\right)_j \quad (S5)$$

provided that the dn/dc contributions of the multicomponent polymer in a single solvent are additive. Using values of $(dn/dc)_{PFS} = 0.253$ mL/g and $(dn/dc)_{POEGMA} = 0.132$ mL/g in ethanol, $(dn/dc)_{PFS} = 0.279$ mL/g and $(dn/dc)_{POEGMA} = 0.143$ mL/g in methanol, and $(dn/dc)_{PFS} = 0.275$ mL/g and $(dn/dc)_{POEGMA} = 0.137$ mL/g in water, we calculated $(dn/dc)_{polymer} = 0.164$ in methanol, 0.153 in the methanol/ethanol mixture (1:4 v/v) and 0.158 mL/g in water. The dn/dc values for POEGMA were determined indirectly by measuring the refractive index of a series of POEGMA solutions of known concentration in each solvent. The dn/dc values for PFS in different solvents were calculated based on the Gladstone-Dale relation:²

$$\left(\frac{dn}{dc}\right)_2 = \left(\frac{dn}{dc}\right)_1 + \frac{n_1 - n_2}{\rho_p} \quad (S6)$$

where 1 and 2 refer to the two solvents and ρ_p refers to the density of PFS (1.6 g/cm³).

The SLS data were plotted as Holtzer-Casassa (HC) plots (Figure 2, main text) of $qR_\theta/\pi M_0 K c$ as a function of q and fitted according to equation S3 to get three parameters of the rod-like micelles: (i) the weight average length of the micelle L_w , (ii) the number of block copolymers per unit length of the micelles, the linear aggregation number, $N_{agg/L}$, and (iii) the radius of the cylinder cross section, R_{SLS} .

In multi-angle dynamic light scattering (DLS), we measure the normalized intensity-intensity time-correlation function $[(g^{(2)}(q, \tau) - B)/B]$, where B is the measured baseline, τ is the decay time. $g^{(2)}(q, \tau)$ is related to the normalized electric field correlation function $g^{(1)}(q, \tau)$ by the Siegert relation:³

$$g^{(2)}(\tau) = 1 + \beta |g^{(1)}(\tau)|^2 \quad (S7)$$

where β is the spatial coherence coefficient of the instrument. The Laplace inversion of $g^{(1)}(q, \tau)$ of scattering objects in a dilute solution can lead to a line-width distribution ($G < \Gamma >$). For a purely diffusive relaxation, for example of spherical particles, Γ is related to the translational diffusive coefficient (D) by $D = (\Gamma/q^2)_{q \rightarrow 0, c \rightarrow 0}$.

To take account of the rigid rod shape of the micelles, we first analyzed the data by CONTIN analysis, with an example of CONTIN plots shown in Figure S10. Here only monomodal distribution of decay time was obtained after CONTIN analysis, thus the apparent

diffusion coefficient at individual scattering angle could be calculated in terms of a cumulant expansion to second order (2-CUM) of the logarithm of $g^{(1)}(\tau)$, using the ALV correlator software:

$$\text{Ln}g^{(1)}(\tau) = -\Gamma_1\tau + \left(\frac{\mu_2}{2!}\right)\tau^2 \quad (\text{S8})$$

where Γ_1 is also known as the first cumulant, μ_2 is the second cumulant. The evolution of Γ_1 is influenced by the translational diffusion coefficient parallel to the rod axis, $D_{\parallel}$, that perpendicular to the rod axis $D_{\perp}$, and the rotational diffusion coefficient, D_r , as a function of the scattering angle. For a dilute solution of rigid rods, when the translational and rotational motions are coupled, and Wilcoxon and Schurr⁴ have shown that Γ/q^2 can be expressed by eq S9:

$$\frac{\Gamma_1}{q^2} = \left[D + 2(D_{\parallel} - D_{\perp}) \cdot \left(\frac{1}{3} - F(qL) \right) + 2L^2 D_r G(qL) \right] \quad (\text{S9})$$

where D is the overall translational diffusion coefficient of the rod, defined as $D = (2 D_{\perp} + D_{\parallel})/3$. $F(qL)$ and $G(qL)$ are universal functions of qL , which are defined in terms of readily evaluated sums:

$$F(qL) \equiv \frac{\text{SUM2}}{\text{SUM1}} \quad (\text{S10})$$

$$G(qL) \equiv \frac{N^{-2}\text{SUM3}}{\text{SUM1}} \quad (\text{S11})$$

where

$$\text{SUM1} \equiv N^2 \frac{1}{(qL)^2} \iint_{-\frac{qL}{2}}^{\frac{qL}{2}} \frac{\sin|x-y|}{|x-y|} dx dy \quad (\text{S12})$$

$$\text{SUM2} \equiv N^2 \frac{1}{(qL)^2} \iint_{-\frac{qL}{2}}^{\frac{qL}{2}} \left\{ \frac{\sin|x-y|}{|x-y|^3} - \frac{\cos|x-y|}{|x-y|^2} \right\} dx dy \quad (\text{S13})$$

$$\text{SUM3} \equiv N^4 \frac{1}{(qL)^4} \iint_{-\frac{qL}{2}}^{\frac{qL}{2}} xy \left\{ \frac{\sin|x-y|}{|x-y|^3} - \frac{\cos|x-y|}{|x-y|^2} \right\} dx dy \quad (\text{S14})$$

with N identical scattering elements arranged in a linear sequence of a thin rigid rod.

The translational and rotational diffusion coefficients can be expressed as a function of the ratio of the rod length to the cross-sectional diameter, L/d , and the solvent viscosity, η_0 .⁵⁻⁷ These values are evaluated according to the boundary element method (BE) developed by Aragon and Flamik,⁸ where the PFS rods are best represented by cylinders with flat caps.

For cylinders with flat caps, the translational diffusion coefficients, $D_{\parallel}$ and $D_{\perp}$, are given by⁹

$$D_{\parallel} = \frac{kT}{4\pi\eta_0 L} \left(2\ln\left(\frac{L}{d}\right) + X_{\parallel} \right) \quad (\text{S15a})$$

$$D_{\perp} = \frac{kT}{4\pi\eta_0 L} \left(\ln\left(\frac{L}{d}\right) + X_{\perp} \right) \quad (\text{S15b})$$

where

$$X_{\parallel}\left(\frac{L}{d}\right) = -0.234963 - \frac{3.14268}{\sqrt{\frac{L}{d}}} + \frac{4.29031}{\frac{L}{d}} + \frac{0.197913}{\left(\frac{L}{d}\right)^2} + \frac{1.96581 \ln\left(\frac{L}{d}\right)}{\left(\frac{L}{d}\right)^2} \quad (\text{S16a})$$

$$X_{\perp}\left(\frac{L}{d}\right) = 0.866049 - \frac{0.650602}{\sqrt{\frac{L}{d}}} + \frac{1.2839}{\frac{L}{d}} - \frac{0.397905}{\left(\frac{L}{d}\right)^2} - \frac{0.18332 \ln\left(\frac{L}{d}\right)}{\left(\frac{L}{d}\right)^2} \quad (\text{S16b})$$

and the rotational diffusion coefficient D_r is given by

$$D_r = \frac{3kT}{\pi\eta_0 L^3} \left(\ln\left(\frac{L}{d}\right) + X_r \right) \quad (\text{S17})$$

where

$$X_r\left(\frac{L}{d}\right) = -0.480483 - \frac{1.40054}{\sqrt{\frac{L}{d}}} - \frac{3.91903}{\frac{L}{d}} - \frac{2.4528}{\left(\frac{L}{d}\right)^3} + \frac{0.587033}{\left(\frac{L}{d}\right)^4} - \frac{2.58127 \ln\left(\frac{L}{d}\right)}{\left(\frac{L}{d}\right)^2} \quad (\text{S18})$$

By varying the value of d (cross-sectional diameter), one can fit the plot of Γ_l/q^2 as a function of qL to get the hydrodynamic radius R_{DLS} for each micelle solution. In this way, we fitted the data for the micelles of different lengths in different solvents (TEM images in Figure 1 and S6) prepared by seeded growth from the micelle fragment seeds obtained by the TA-approach.

6. Tests of the thermoresponse of PFS₂₆-b-POEGMA₁₆₃ micelles in water

A temperature-dependent turbidity test was carried out on POEGMA₁₆₃ homopolymer in water by monitoring the transmittance light at 500 nm. An aqueous solution (5 mg/mL) of POEGMA₁₆₃-N₃ was examined by UV-Vis absorbance measurements at 23 °C, 35 °C, 38 °C, 40 °C, 41 °C, 42 °C and 45 °C. The solution in the cuvette took ca. 2 min to reach the target temperature. Then the sample was equilibrated at that temperature for an additional 2 min before acquiring a signal. Figure S8A shows the transmittance of light as a function of temperature and indicates a cloud point of 40.5 °C. The thermoresponse of a more dilute PEOGMA (0.3 mg/mL) solution was also examined by light scattering: the scattered light intensity at 90° was recorded for the heating and cooling cycles. The sample was equilibrated at each temperature for 2 min

before acquiring signals. Figure S8B shows the light intensity as a function of temperature and indicates an LCST at ca. 43 °C. A CONTIN plot (90 ° scattering angle) of the DLS data at 22.3 °C indicates individual molecules, whereas above the LCST at 44.5 °C, one sees only aggregates due to phase separation.

Then temperature-dependent multi-angle light scattering measurements were carried out with the shortest micelle sample in water ($L_w = 210$ nm, $m_{\text{unimer}}/m_{\text{seed}} = 2.2$, $c = 1.2$ µg/mL) at 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, and 50 °C for the heating cycle, then 49, 47, 45, 43, 41, 39, 37, 35, 33, 31 and 22.5 °C (room temperature) for the cooling cycle. The sample in the sample chamber took ca. 10 min to reach the target temperature. Then the sample was equilibrated at that temperature for 30 min before acquiring signals. SLS and DLS signals were recorded simultaneously. For each temperature, each multi-angle measurement took ca. 30 mins. Autocorrelation decay profiles and corresponding CONTIN plots (at 90°) for two different temperatures are presented in Figure S10. For SLS data, we also calculated the radius of gyration $\langle R_g^2 \rangle^{1/2}$ and the weight-averaged molecular weight (M_w) at each temperature from a Zimm plot (eq S19)

$$\frac{Kc}{R_\theta} = \frac{1 + \frac{\langle R_g^2 \rangle q^2}{3}}{M_w} \quad (\text{S19})$$

We also calculated values of R_{SLS} at each temperature. In contrast to the changes in R_{DLS} , values of $R_{\text{SLS}} = 10$ nm remained constant over the temperature range of 23 to 50 °C, emphasizing both the challenge in measuring a change in such a small value and the dominant contribution of the mass of the PFS core to this parameter.

7. Calculating the grafting energy of each POEGMA₁₆₃ chain on the PFS₂₆-b-POEGMA₁₆₃ cylindrical brushes in water

A recent paper¹⁰ described the calculation of the free energy per chain of a polymer brush on a planar surface in order to determine the optimum grafting density of polymers like polyethylene glycol (PEG) to resist protein adsorption. While it is well documented that the adsorption of proteins on such a polymer brush decreases as the grafting density increases, there are examples in the literature where the protein adsorption increases when the grafting density becomes too high. This paper suggests that, in addition to the steric effect of the hydrated water-soluble polymers, fluctuations in the dimensions of individual chains play an important role in

resisting protein adsorption. The paper suggests that the optimum grafting density corresponds to a free energy of about 10 kT per chain.

The model is based on the idea that in a planar brush, individual chains can be treated as though they are confined to a cylindrical space (i.e., a tube). The free energy of the chain A depends on two entropic terms, describing the free volume and the elastic energy. For individual chains in a polymer brush confined to a cylindrical space, the brush height L_o is related to the Kuhn length of the brush polymer a and the grafting density σ by the expression

$$L_o = \pi^{1/2} \left(\frac{a}{2} \right) \sigma^{1/2} L_{\text{contour}} \quad (\text{S20})$$

where L_{contour} is the contour length of the grafted chains. For a given polymer, a and L_{contour} are constant, so that the brush height L_o depends only on the grafting density.

The minimum free energy of a grafted chain (A_{min}) is given by the expression

$$\frac{A_{\text{min}}}{kT} = \left(\frac{27a}{16} \right)^{1/3} \sigma^{2/3} L_{\text{contour}} \quad (\text{S21})$$

Although this expression is derived for cylindrical confinement, it was also applied to PEG chains on a thermally responsive spherical microgel. By varying the temperature to shrink the microgel, the author was able to examine how the brush height L_o varied with the grafting density σ . In this spirit, we apply the model to our cylindrical brush, ignoring the effects of curvature on the calculated free energy.

For the grafted POEGMA₁₆₃ brushes we studied here, the contour length was calculated from $L_{\text{contour}} = 2Nl \sin(\theta/2)$ (N is the number of repeat units, l is the length of a C-C bond (0.154 nm), and θ is the bond angle (109°)). The brush height ($L_o = 20$ nm) was taken to be the difference between the cross section hydrodynamic radius ($R_{\text{DLS}} = 26.5$ nm) and the micelle core radius ($R_{\text{core}} = 6.5$ nm). Introducing these values of L_o and L_{contour} into eq S20, we find a Kuhn length $a = 2.0$ nm. In combination with $\sigma = 0.12$ chains/nm², we obtained a value of free energy per chain of 14.6 kT.

ADDITIONAL TABLES

Table S1. Summary of the polymer characteristics

Polymers	Theoretical M_n^a (g/mol)	$M_n^{\text{NMR } b}$ (g/mol)	M_n^{GPC} (g/mol)	M_n^{MALDI} (g/mol)	$\bar{D}^c$
PFS ₂₆ -alkyne	6.4 K	-	6.0 K	6.8 K	1.03
POEGMA ₁₆₃ -N ₃	16.7 K	35.8 K	25 K	-	1.30
PFS ₂₆ - <i>b</i> -POEGMA ₁₆₃	23.1 K	42.1 K	31.6 K	-	1.28

^a Theoretical molecular weight was calculated by the equation:

$$M_n = [M]/[I] \times M_{\text{monomer}} \times \text{Monomer Conversion} + M_{\text{Initiator}}$$

^b Calculated from DP

^c Determined by GPC

Table S2. Summary of micelle preparation and shape by PFS₂₆-*b*-POEGMA₁₆₃

Solvent ^a	Assembly approach	Solution appearance	Assembly results ^b
Methanol	DA ^c	Clear	S + SR
	TA ^d	Clear	L
Ethanol	DA	Turbid	S + SR
	TA	Turbid	F
Methanol:Ethanol = 1:4	DA	Clear	S+SR
	TA	Clear	F
2-Propanol	DA	Precipitate	-
	TA	Precipitate	-

^a The BCP concentration of each solution is 0.2 mg/mL.

^b S: Spherical micelles, SR: short rod-like micelles, L: lenticular micelles, F: long fiber-like micelles of uniform width.

^c Direct self-assembly

^d THF-assisted self-assembly

Table S3. Summary of the characteristics determined by TEM of the micelles prepared by seeded growth of PFS₂₆-*b*-POEGMA₁₆₃ in different solvents

Solvent	Assembly approach	$m_{\text{unimer}}/m_{\text{seeds}}$	L_n (nm)	L_w (nm)	L_w/L_n
Methanol:Ethanol = 1:4	DA ^a	Seed	59.8	65.9	1.10
		1.7	136	142	1.04
		4.3	232	242	1.04
		8.1	389	397	1.02
	TA ^a	Seed	65	74	1.15
		2.2	200	208	1.04
		4.3	312	321	1.03
		6.9	500	510	1.02
Methanol	DA ^a	Seed	37.1	38.5	1.04
		1.9	151	164	1.08
		4.2	273	284	1.04
		8.3	446	455	1.02
	TA ^b	2.2	204	211	1.04
		4.3	325	330	1.02
		6.9	475	482	1.01
Water	TA ^b	2.2	200	207	1.03
		4.3	300	306	1.02
		6.9	477	484	1.02

^a. Seeded growth in that solvent

^b. Seeded growth in methanol:ethanol = 1:4 v/v followed by transfer to methanol or water.

SUPPORTING FIGURES

Figure S1. MALDI-TOF mass spectrum of alkyne-terminated PFS₂₆ homopolymer. M_n = 6800 Da, M_w = 7000 Da, PDI = 1.03

Figure S2. ¹H-NMR of POEGMA₁₆₃-N₃ (in CDCl₃). End group analysis did not give an accurate DP due to overlap of signals from the initiator and polymer

Figure S3. GPC curves in THF before (black lines) and after (blue lines) the click coupling reaction of PFS-alkyne and POEGMA- N_3 and after purification of the BCP (red lines). (A) RI signal and (B) UV-Vis signal (UV-Vis detector wavelength: 450 nm)

Figure S4. $^1\text{H-NMR}$ of $\text{PFS}_{26}\text{-}b\text{-POEGMA}_{163}$ (in CD_2Cl_2). Comparing the integration of protons from the Cp rings (B) and methylene groups (D) gave a block ratio of 1: 6.3, from which we calculate the DP of POEGMA = $26 \times 6.3 = 163$.

Figure S5. TEM images of PFS₂₆-*b*-POEGMA₁₆₃ self-assembled in methanol (A,D), ethanol (B,E) and methanol/ethanol mixture (v:v = 1:4) (C,F) by the DA approach (A,B,C) or the TA approach (D,E,F). Scale bars: 500 nm. Insets: magnification of a portion of the corresponding images, scale bar: 100 nm. Red circles indicate the spherical micelles.

Figure S6. TEM images and length histograms of the $PFS_{26}\text{-}b\text{-}POEGMA_{163}$ micelles in methanol by seeded growth after aging for 7 days with DA-approach-generated seeds. (A) Seed micelles after sonication of micelles prepared by DA approach. (B-D) Uniform rod-like micelles of different lengths with spherical micelles (indicated by the red circles). (E-H) Length histograms of the micelles shown in parts A-D. (E) $L_n = 37.1$ nm, $L_w = 38.5$ nm, $L_w/L_n = 1.04$. (F) $L_n = 151.2$ nm, $L_w = 163.8$ nm, $L_w/L_n = 1.08$. (G) $L_n = 272.5$ nm, $L_w = 283.6$ nm, $L_w/L_n = 1.04$. (H) $L_n = 446.1$ nm, $L_w = 454.9$ nm, $L_w/L_n = 1.02$. (I) Number average length L_n versus the ratio of the amount of unimer to seeds for the micelles showed in parts A-D. The dashed line represents the predicted maximum lengths based on eq. S2. The fact that the data points lie above this line indicate that the spherical micelles in the seed solution were unable to initiate CDSA. Scale bars: 500 nm

Figure S7. TEM images and length histograms of the PFS₂₆-b-POEGMA₁₆₃ micelles after they were dispersed in methanol (A-D) and in water (E-H). (D) Length histograms of the micelles shown in panel A-C. Black: $m_{\text{unimer}}/m_{\text{seed}} = 2.2$, $L_n = 203.6$ nm, $L_w = 210.8$ nm, $L_w/L_n = 1.04$. Red: $m_{\text{unimer}}/m_{\text{seed}} = 4.3$, $L_n = 325.2$ nm, $L_w = 330.1$ nm, $L_w/L_n = 1.02$. Blue: $m_{\text{unimer}}/m_{\text{seed}} = 6.9$, $L_n = 475.2$ nm, $L_w = 482.1$ nm, $L_w/L_n = 1.01$. (H) Length histograms of the micelles shown in panel E-G. Black: $m_{\text{unimer}}/m_{\text{seed}} = 2.2$, $L_n = 200.2$ nm, $L_w = 206.6$ nm, $L_w/L_n = 1.03$. Red: $m_{\text{unimer}}/m_{\text{seed}} = 4.3$, $L_n = 300.3$ nm, $L_w = 305.8$ nm, $L_w/L_n = 1.02$. Blue: $m_{\text{unimer}}/m_{\text{seed}} = 6.9$, $L_n = 477.0$ nm, $L_w = 484.3$ nm, $L_w/L_n = 1.02$. Scale bars: 500 nm.

Figure S8. (A) UV-Vis turbidity measurement of an aqueous solution of POEGMA₁₆₃-N₃ (5 mg/mL) at various temperatures (the red line indicates the cloud point at 40.5 °C). (B) Scattering light intensity at 90° of a dilute (0.3 mg/mL) aqueous solution of POEGMA₁₆₃-N₃ as a function of temperature (heating cycle: black squares, cooling cycle: red dots). Inset: representative intensity-averaged CONTIN plots show phase separation and aggregation at 44.5 °C but individual molecules at 22.3 °C.

Figure S9. High magnification TEM image (A) and width histogram (B) of the PFS₂₆-*b*-POEGMA₁₆₃ micelles ($m_{\text{unimer}}/m_{\text{seed}} = 6.9$) deposited from water. $W_n = 13.1$ nm, $W_w = 13.3$ nm, $W_w/W_n = 1.01$. Scale bar: 50 nm

Figure S10. 90° DLS autocorrelation decay curves at 22 °C (A) and 50 °C (C) with their corresponding CONTIN plots (B: 22 °C, D: 50 °C) of PFS₂₆-*b*-POEGMA₁₆₃ micelles in water (Figure S7E) after they were equilibrated at the two temperatures for 30 mins.

REFERENCES

- (1) Zhang, M.; Rupa, P. A.; Feng, C.; Lin, K.; Lunn, D. J.; Oliver, A.; Nunns, A.; Whittell, G. R.; Manners, I.; Winnik, M. A. *Macromolecules* **2013**, *46* (4), 1296–1304.
- (2) Gladstone, J. H. *Researches on the refraction, dispersion, and sensitiveness of liquids.*; [London], 1863.
- (3) Zero, K.; Pecora, R. In *Dynamic Light Scattering*; Springer, Boston, MA, 1985; pp 59–83.
- (4) Wilcoxon, J.; Schurr, J. M. *Biopolymers* **1983**, *22* (3), 849–867.
- (5) Broersma, S. J. *J. Chem. Phys.* **1960**, *32* (6), 1626–1631.
- (6) Broersma, S. J. *J. Chem. Phys.* **1960**, *32* (6), 1632–1635.
- (7) Broersma, S. J. *J. Chem. Phys.* **1981**, *74* (12), 6989–6990.
- (8) Aragon, S. R.; Flamik, D. *Macromolecules* **2009**, *42* (16), 6290–6299.
- (9) Guerin, G.; Qi, F.; Cambridge, G.; Manners, I.; Winnik, M. A. *J. Phys. Chem. B* **2012**, *116* (14), 4328–4337.
- (10) Wu, C. *Chin. J. Polym. Sci.* **2014**, *32* (11), 1575–1580.