Supporting Information
A stepwise “micellization–crystallization” route to oblate ellipsoidal, cylindrical, and bilayer micelles with polyethylene cores in water

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Experimental section

Materials. AE diblock copolymers were synthesized using a combination of anionic and RAFT polymerizations coupled with hydrogenation. First, sequential anionic polymerization of butadiene in nonpolar cyclohexane at 40 °C with sec-butyllithium as the initiator and addition of excessive ethylene oxide afforded a ω-hydroxyl terminated poly(1,4-butadiene) (PB-OH). $M_n$ ($^1$H NMR, end-group analysis): 3.1 kg·mol$^{-1}$, 1,4-addition ($^1$H NMR): 91%, $D$: 1.06 (GPC, in chloroform, relative to PS standards). Second, the PB-OH was hydrogenated with Pt/SiO$_2$ catalyst in cyclohexane at 80 °C to afford a ω-hydroxyl terminated polyethylene (PE-OH). Conversion ($^1$H NMR): > 99%, $M_n$ ($^1$H NMR): 3.3 kg·mol$^{-1}$, $D$: 1.16 (GPC, in 1,2,4-trichlorobenzene at 135 °C, relative to PS standards). No apparent loss of hydroxyls was detected during the hydrogenation step. Afterwards, a trithiocarbonate RAFT chain transfer agent (CTA) $^1$ was attached to the ω-terminus of PE via acyl-chloride-mediated esterification. Finally, $N,N$-dimethyl acrylamide was radically polymerized in the presence of the PE-CTA in toluene at 75 °C with AIBN as the initiator to afford PDMA–PE (AE) diblock copolymers with different lengths of PDMA blocks. The conversions of DMA were typically larger than 95%. AE diblock copolymers were isolated by twice precipitations into hexanes (ice cold) followed by filtration or centrifugation, and then the remaining volatiles were removed under vacuum to afford dry powders as the product.

Preparation of micellar solutions. A pressure vessel was charged with dry AE diblock copolymers and DI water to form a solution with polymer content of 1.0 wt %, as well as a stir bar. The mixture was degassed by Argon bubbling for 30 min before being placed in a preheated 120 °C oil bath. The temperature was held at 120 ± 1 °C for at least 1 week, and then the mixture was allowed to cool to ambient temperature at a rate of ca. 1 °C min$^{-1}$.

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Small-angle and wide-angle X-ray scattering (SAXS and WAXS). The SAXS and WAXS measurement was done at the 5-ID-D station of the Advanced Photon Source at Argonne National Laboratory. The energy of the synchrotron X-ray source was 17 keV, which corresponded to a wavelength of 0.729 Å. The sample-to-detector distance was 4000 mm (SAXS) and 236 mm (WAXS) to cover a $q$-range of 0.0065 – 0.17 and 0.62 – 4.6 Å$^{-1}$, respectively. The 2-D scattering images collected on the MAR (SAXS) and Roper (WAXS) CCD detector were azimuthally integrated into 1-D profiles of $I$ vs $q$ using the data reduction software FIT2D. Bulk samples for SAXS were melt pressed and encapsulated inside hermetically sealed aluminum pans, and the temperature was controlled within ± 0.2 °C with a Linkam DSC stage. The thickness of the samples were estimated to be 2.0 ± 0.1 mm. No background correction was done for the SAXS profiles. Solution samples for WAXS were loaded into quartz capillary tubes (Charles Supper Co., 2.0 mm o.d.), and the measurement was done at ambient temperatures (ca. 22 °C). Scattering profiles from the capillary tube and solvent (DI water) were also collected and used to normalize the WAXS profiles of the micellar solutions.

Cryo-TEM. Samples for cryo-TEM were prepared using a home-built controlled environment vitrification system (CEVS) at 22 °C. An aliquot of the micelle solution (~ 8 μL) was loaded onto a lacey carbon support film that was held by a pair of tweezers in the CEVS filled with saturated water vapor. Excess solution was blotted away using a piece of filter paper to form thin films (ca. 100 – 300 nm in thickness) spanning the holes of the lacey carbon. After a 15 s delay, the grid was quickly plunged into liquid ethane (at ~ 90 K) that was cooled by surrounding liquid nitrogen. The vitrified samples were stored in liquid nitrogen until they were transferred onto Gatan 626 cryogenic sample holder and examined in a JEOL 1210 TEM at about –177 °C. The accelerating voltage was 120 kV. Images were acquired using a Gatan 724 multiscan CCD camera and processed with Digital Micrographs version 3.3.1. The phase contrast was enhanced by imaging at 8–20 μm underfocus.

Small-angle neutron scattering (SANS). SANS measurement was carried out on the NG-7 30 m beamline of the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST). Two setups – a wavelength of 8.0 Å with sample-to-detector distance of 15.3 m and a wavelength of 7.0 Å with sample-to-detector distances of 13.0 m, 3.0 m, and 1.0 m – were employed to cover a $q$ range of 0.0009 – 0.38 Å$^{-1}$. Samples for measurement at 25 °C were loaded into NIST quartz cells with thickness of 1.0 mm. Samples for measurement at 120 °C were held in NIST pressure cells with thickness of 4.0 mm, inside which a quartz spacer that was ca. 1.5 mm thick was placed to form a solution with a thickness of ca. 2.5 mm in the beam path. The pressure cells were pressurized with 32 psi of N$_2$ to minimize the formation of air bubbles at 120 °C. The total counts of neutrons on a image were at least 10,000 to ensure sufficiently high signal-to-noise ratio. The raw data was corrected for
blocked beam scattering, sample transmission, empty cell scattering, and detector efficiency, and then
converted into absolute scale using direct beam flux method. Further, the scattering from solvent was
subtracted to give the pure scatterings from suspended particles. The SANS data was reduced and
analyzed using the NIST software package version 7.04b in Igor Pro.\textsuperscript{2}

\textit{Model-independent analysis.} In the low \(q\) region \((9\times10^{-4} < q < 5\times10^{-3}\ \text{Å}^{-1})\), we calculated the radius of
gyration \((R_g)\) of the suspended particles using the Guinier plot, which involves plotting \(\ln[I(q)]\) vs \(q^2\)
following equation S1.

\[ \ln[I(q)] = \ln[I(q = 0)] - \frac{q^2}{3} R_g^2 \]  

(S1)

Further, we obtained the volume \((V_p)\) of the suspended particles using the extrapolated \(\ln[I(q = 0)]\)
following equation S2.

\[ \ln[I(q = 0)] = \Phi(\Delta\rho)^2 V_p \]  

(S2)

in which \(\Phi\) is the total volume fraction of the suspended particles in the solution, and \(\Delta\rho\) is the contrast
between the suspended particles and the solvent. We calculated \(\Phi\) from the estimated scattering
invariant, \(Q\) (as defined in equation S3), using the relation as shown in equation S4. For the estimation
of \(Q\), the absolute scattering intensity, \(I(q)\), was extrapolated to \(10^{-5}\ \text{Å}^{-1}\) in the low \(q\) region with the
Guinier plot, and \(10\ \text{Å}^{-1}\) in the high \(q\) region with the Porod plot \((\text{vide infra})\). The difference between
the estimated \(Q\) over the range of \(10^{-5} - 10\ \text{Å}^{-1}\) and the calculated \(Q\) over the measured \(q\) range (i.e.,
\(0.0009 - 0.38\ \text{Å}^{-1}\)) was less than 3.0%.

\[ Q = \int_0^\infty q^2 I(q) dq \]  

(S3)

\[ Q = 2\pi^2(\Delta\rho)^2 \Phi(1-\Phi) \]  

(S4)

In the high \(q\) region \((8\times10^{-2} < q < 3\times10^{-1}\ \text{Å}^{-1})\), the scattering intensity, \(I(q)\), decays as \(q^{-4}\), which
indicates sharp interfaces between the suspended particles and the solvent. Using the Porod constant, \(C_p\),
as defined in equation S5, we calculated the specific surface area (i.e., the surface area per unit volume
of sample), \(S_v\), following equation S6.

\[ \Phi = \int_0^\infty \frac{2\pi^2 q^2 (\Delta\rho)^2 (1-\Phi) I(q)}{Q} dq \]  

(S5)

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\[ S_v = \frac{2\pi^2(\Delta\rho)^2 \Phi(q)}{Q} dq \]  

(S6)

\[ C_p = \lim_{q \to \infty} q^4 I(q) \quad \text{(S5)} \]

\[ C_p = 2\pi \cdot S_v (\Delta \rho)^2 \quad \text{(S6)} \]

\( S_v \) is related with the average particle dimensions: \( S_v = 6\Phi/D \) for spheres with the diameter of D, \( S_v = 4\Phi/D \) for infinitely long cylinders with the diameter of the cross section of D, and \( S_v = 2\Phi/D \) for vesicles with the wall thickness of D.

In addition, the interfacial area per chain, \( a_0 \), of the micelles can be calculated from \( S_v \) using equation S7.

\[ a_0 = \frac{S_v}{\Phi} \cdot \frac{M_n}{\rho \cdot N_A} \quad \text{(S7)} \]

in which \( M_n \) is the number average molecular weight of the core-forming blocks (PE) of the micelles, \( \rho \) is the density, and \( N_A \) is Avogadro’s number.

**Fitting the absolute scattering intensity with models.** The scattering profiles of AE(1.4-3) micelles in D\(_2\)O at 25 and 120 °C were also fitted with the form factors of particles with different shapes to get quantitative information about their packing characteristics. The models included (1) spheres with radii of Gaussian distribution, (2) randomly orientated disks whose thickness is monodisperse while the radii follow Schulz distribution, and (3) randomly orientated oblate ellipsoids whose minor radii are monodisperse while the major radii follow Gaussian distribution. Smearing of the form factors as limited by the instrument resolution was also included using the NIST software package version 7.04b. ²

The absolute scattering intensity of spheres with radii of Gaussian distribution is shown as equation S8.

\[ I(q) = N_0 (\Delta \rho)^2 \int_0^\infty \frac{\sigma}{2\pi} \exp \left[ -\frac{1}{2\sigma^2} \left( R_c - R_{\text{avg}} \right)^2 \right] f(R_c) V_{\text{sph}}^2 \cdot F^2(qR_c) dR_c \quad \text{(S8)} \]

in which \( N_0 \) is the total number of particles per unit volume, \( \Delta \rho \) is the contrast between the suspended particles and the solvent, \( f(R_c) \) is normalized Gaussian distribution as described in equation S9, \( V_{\text{sph}} \) is the volume of spheres with radius of \( R_c \) (i.e., \( 4/3\pi R_c^3 \)), and \( F(R_c) \) is the scattering amplitude for a sphere as described in equation S10.

\[ f(R_c) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2\sigma^2} \left( R_c - R_{\text{avg}} \right)^2 \right] \quad \text{(S9)} \]
\[ F(qR_c) = \frac{\sin(qR_c) - (qR_c)\cos(qR_c)}{(qR_c)^3} \quad (S10) \]

The absolute scattering intensity of randomly orientated disks whose thickness \((L)\) are monodisperse while the radii \((R_c)\) follow Schulz distribution is shown as equation \(S11\).

\[ I(q) = N_0(\Delta \rho)^2 \left[ \frac{Z+1}{Z+2} \right] x f_z(R_c) dR_c \int_0^{\pi/2} F_{cyl}^2(q,\alpha) \sin \alpha d\alpha \quad (S11) \]

in which \(f_z(R_c)\) is the normalized Schulz distribution of the radius as described in equation \(S12\).

\[ f_z(R_c) = (z+1)^{z+1} x z \frac{\exp[-(z+1)x]}{R_{avg} \Gamma(z+1)} \quad (S12) \]

\(R_{avg}\) is the mean radius and \(x = R_c/R_{avg}\). \(z\) is related to the polydispersity by \(z = (R_{avg}/\sigma)^2 - 1\), and \(\sigma^2\) is the variance of the distribution.

\(F(q,\alpha)\) is the scattering amplitude for orientationally averaged rigid cylinders as described in equation \(S13\), and \(\alpha\) is defined as the angle between the cylinder axis and the scattering vector, \(q\).

\[ F_{cyl}(q,\alpha) = 2V_{cyl} \cdot j_0(qL\cos \alpha) \frac{J_1(qR_c \sin \alpha)}{qR_c \sin \alpha} \quad (S13) \]

in which \(V_{cyl}\) is the volume of a cylinder with radius of \(R_c\) and length of \(L\), \(j_0(x)\) is defined as \(\sin x/x\), and \(J_1(x)\) is the first order Bessel function.

The absolute scattering intensity of randomly orientated oblate ellipsoids with monodisperse minor radius \((R_a)\) and the major radius \((R_b)\) of Gaussian size distribution is shown as equation \(S14\).

\[ I(q) = N_0(\Delta \rho)^2 \int_0^{\infty} f(R_b) V_{ell}^2 dR_b \int_0^{\pi/2} F^2(qR_{om}) \sin \alpha d\alpha \quad (S14) \]

in which \(V_{ell}\) is the volume of an oblate ellipsoid with minor radius of \(R_a\) and major radius of \(R_b\) (i.e., \(4/3\pi R_a R_b^2\)), \(R_{om}\) is the orientation-dependent radius as described in \(S15\), and \(\alpha\) is defined as the angle between the ellipsoid axis and the scattering vector, \(q\).

\[ R_{om} = R_b \sqrt{\sin^2 \alpha + \cos^2 \alpha \left( \frac{R_a}{R_b} \right)^2} \quad (S15) \]
The scattering profiles of AE(1.0-3) micelles in D₂O at 25 °C were fitted with a model of non-interacting flexible cylinders, whose cross-sectional radii follow a Schulz distribution, as described by Pedersen et al.³ and Chen et al.⁴

**Shear rheometry.** Steady and small-amplitude oscillatory shear measurements were performed using a AR-G2 rheometer (TA Instruments). A standard Couette cell was used – the length was 42 mm, and the gap was 1 mm between the inner cylinder (with a radius of 14 mm) and outer cylinder (with a radius of 15 mm). About 12 mL of the sample was loaded into the cup to fill the gap. The temperature was controlled at 20.0 ± 0.1 °C. The assembly was covered with water-soaked foams to minimize the evaporation of water. The frequency dependence of storage and loss moduli (G’ and G”) was measured by linear dynamic (i.e., oscillatory) frequency sweeps from 100 to 0.01 rad s⁻¹ at strains (e.g., 25%) that are located in the linear regime, which are determined by dynamic strain sweep experiments. The oscillatory torque of the data shown was at least 3 times as large as the limit of the rheometer (0.003 μN m). Steady shear measurements were carried out with the shear rate increasing from 0.01 to 500 s⁻¹. To minimize the transient effects of the sample, pre-shearing of 180 s, 60 s, and 30 s was employed before data collection for shear rates in the ranges of 0.01 – 0.1, 0.1 – 1.0, and 1.0 – 500 s⁻¹, respectively. The steady shear torque of the data shown was at least 10 times as large as the limit of the rheometer (0.01 μN m).

**Figure S1.** Synchrotron SAXS data for self-assembled AE bulk samples acquired at 140 °C. All samples were annealed for at least 5 min before data were collected. From bottom to top (a) AE(0.7-3), disordered; (b) AE(0.8-3), hexagonally packed cylinders of PDMA in a PE matrix; (c) AE(1.0-3), hexagonally packed cylinders of PDMA in a PE matrix; (d) AE(1.4-3), lamellae; (e) AE(2.2-3), lamellae; (f) AE(4.0-3), hexagonally packed cylinders of PE in a PDMA matrix; (g) AE(5.9-3), hexagonally packed cylinders of PE in a PDMA matrix; (h) AE(9.3-3), body-centered cubic spheres of PE in a PDMA matrix.
Figure S2. Temperature dependence of $\chi$ determined through the change in the domain spacing ($D_{\text{lam}}$) of a lamellae-forming sample, AE(2.2-3), between 110 and 160 °C. A linear fit to the data gave: $\chi(T) = \frac{221}{T} - 0.24$ ($R^2 = 0.99$). This equation gives $\chi @ 140 ^\circ C = 0.29$, indicating PE and PDMA are moderately segregated at this temperature.
Figure S3. Cryo-TEM images of AE(1.4-3) 0.5 wt % solution prepared by direct dissolution. There existed various conformations of disk-like or oblate ellipsoidal micelles, as the “edge-on” pointed by black circles, “face-on” by black arrows, and others in between.
Figure S4. Cryo-TEM images of AE(2.2-3) 0.5 wt % solution prepared by direct dissolution. There existed various conformations of disk-like or oblate ellipsoidal micelles, as the “edge-on” pointed by black circles, “face-on” by black arrows, and others in between.
Figure S5. Cryo-TEM images of AE(23-3) 0.5 wt % solution prepared by direct dissolution. There existed various conformations of disk-like or oblate ellipsoidal micelles, as the “edge-on” pointed by black circles, “face-on” by black arrows, and others in between. The black arrow head in (a) denotes surface ice contamination.
Figure S6. Cryo-TEM images taken from 0.5 wt % AE(0.8-3) in water at a low (a) and high (b) magnification. Wormlike micelles appeared to be the predominant morphology and some vesicles coexisted.
Figure S7. Simulation of the optical density profile across the core of a “wormlike” micelle with circular (diameter = 20 nm) and square cross-section (side length = 20 nm). A continuous profile was expected for a wormlike micelle with circular cores. In contrast, there was a step change at the interface and the optical density was constant over the entire hydrophobic domain for a 1-D object with square cross section. The assumptions include (i) the contrast only come from the mass-thickness difference, and (ii) the wormlike micelles have uniform electron density over the cores.
Figure S8. DSC curves of a 2.0 wt % wormlike micellar dispersion of AE(1.0-3) in water. The sample was heated and cooled at a rate of 10.0 °C/min between 20 and 120 °C. Shown are the second heating and cooling scans.

Figure S9. Synchrotron WAXS data of a 2.0 wt % wormlike micellar dispersion of AE(1.0-3) in water at 25 °C. We observed two diffraction peaks at 1.51 and 1.67 Å⁻¹, which were indexed to be the (110) and (200) reflections of the orthorhombic crystal lattice of PE, respectively. This result supported the semicrystalline nature of the wormlike micelles, and the nanocrystals of PE micellar cores existed in the same form as that most commonly observed in bulk PE.
Figure S10. SANS profile of AE(1.4-3) spheres dispersed in D$_2$O at 120 °C (open squares), data modeling assuming an ensemble of non-interacting simple spheres without the contribution of PDMA corona (solid line), and data modeling assuming an ensemble of non-interacting core-shell spherical particles with the contribution of PDMA (dash dot line). The first two curves are reproduced from Figure 2(b). This plot suggests the contribution of the swollen PDMA corona chains are insignificant in the spherical micelles from AE(1.4-3), which has the largest PDMA composition among the three samples investigated by SANS. Therefore, it is reasonable to treat the SANS data without the specific consideration of the contribution of PDMA corona.

We followed the model developed by Pedersen et al when calculating the contribution of PDMA.\(^5\) Besides the self-correlation of the core, three terms were also included in the form factor: the self-correlation of the corona chains, the cross term between the sphere and the corona chains, and the cross term between different corona chains. Individual swollen PDMA molecules were assumed to be Gaussian chains, and the radial density distribution function of the PDMA corona followed a linear combination of two cubic $b$ spline functions. In the calculation, the width of the corona profile (corresponding to the difference between the radius of the overall micelle and that of the micellar core) was chosen to be twice as that of the $R_g$ of PDMA, and the fitting parameter of the two spline functions was 1.$^6$ We calculated the contribution of PDMA and added it to the curve modeled without PDMA (solid line) to obtain that modeled with PDMA (dash dot line) in Figure S10.

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