Transforming Spherical Block Polyelectrolyte Micelles into Free-Suspending Films via DNA Complexation Induced Structural Anisotropy

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S1. Materials and instruments:

Materials and sample preparation:

Poly(ethylene oxide)-b-poly(2-vinylpyridine)-b-polystyrene triblock copolymer (PEO_{71}-$P2VP_{12}$-PS_{29}; M_w/M_n = 1.10; the subscriptions represent degrees of polymerization for respective blocks) was purchased from Polymer Source Inc. Salmon sperm single stranded DNA (ssDNA, 200 nucleotides) was purchased from Genmed Scientific Inc. U.S.A and used without further purification. DMF (Shanghai Chem. Reg. Co.) of analytical purity was purified through desiccation and distillation. *N*-butyl iodide (Aldrich) of analytical purity was used as obtained.

PEO_{71}-$P2VP_{12}$-PS_{29} was fully quaternized by *N*-butyl iodide to prepare PEO_{71}-$QP2VP_{12}$-PS_{29}. For the quaterization reaction, PEO_{71}-$P2VP_{12}$-PS_{29} (at the concentration of 0.1 mg/mL) was mixed with 10-fold molar excess of *N*-butyl iodide in *N,N*- dimethylformamide (DMF). The mixture was stirred at room temperature for 24 hours. Then, the resultant solution was diluted by water and then dialyzed against water (using dialytic bags with 3,500 cut-off membrane) for several days to remove DMF and excess *N*-butyl iodide completely. The quaternized triblock copolymer formed micelles in water. The micellar solution was further diluted by distilled water to a copolymer concentration of 0.01 mg/ml. The intensity-average hydrodynamic radius, $\langle R_h \rangle$, of the micelles (at 0.01 mg/mL) was determined by dynamic light scattering (DLS) to be 10.5 nm (Fig. S1a). The apparent molar mass and average aggregation number, Nagg, of the triblock copolymer micelles were 1.1×10^5 g/mol and 15, as determined by static light scattering (SLS) measurements. The conditions for the DLS and SLS measurements were given below.

For the preparation of ssDNA/micelle complex, the ssDNA was dissolved in distilled water at a concentration of 0.01mg/mL. Then, the ssDNA solution was mixed with the micelle solution. The number ratio of ssDNA chains to micelles in the final mixture solution was 1:1.13. The resultant mixture solution was stable since no precipitates were found after storing for four weeks.

Transmission Electron Microscopy (TEM):

Philips CM120 transmission electron microscope was used for TEM observations. TEM specimens were prepared by placing a drop of a solution on a copper grid which was then immediately frozen in liquid nitrogen and subsequently dried under vacuum at -60 ℃ for 72 hours to avoid any changes in the morphologies that may happen during drying the TEM specimens. For the staining, TEM specimens were exposed to vapor of 1% RuO_4(aq) for 2 hours.

Dynamic/Static Light Scattering (DLS/SLS) measurements:
DLS/SLS measurements were performed on a modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and ADLAS DPY425 solid-state laser (output power = 22 mv at λ = 632.8 nm). To protect the instrument, the solutions were filtered by 800 nm Millipore LCR hydrophilic Teflon filters before measurements. All the DLS measurements were performed at the scattering angle of 90° and temperature of 25℃. An ALV-5000 laser light scattering spectrometer was used for SLS measurements. All the solutions were filtered through 0.8 μm Millipore filters. The measurements were conducted at a scattering-angle (θ) range from 15° to 150° with an angular step of 5° . In the present study, the concentration of the micelle solution was very low (10^{-5} g/mL) so that the extrapolation of $C \rightarrow 0$ was unnecessary (*Langmuir* 2003, 19, 10989; *Macromolecules*, 2000, 33, 6340). dn/dC was determined by a Jianke differential refractometer (Jianke Instrument, Ltd.) to be 1.84 x 10^{-4} dm^3/g.

Small Angle X-ray Scattering (SAXS):
For SAXS measurements, 10 mg/mL sample solution (obtained by concentrating the original complex solution at room temperature under vacuum) was sealed in a 0.5 mm capillary tube and measured at room tempreture for 1 hour using a Bruker NanoSTAR SAXS instrument. The intensity profile was output as the plot of the scattering intersity (I) vs. the scattering vector, $q = 4\pi/\lambda \sin(\theta/2)$ (θ = scattering angle, λ = 0.154 nm).

Atomic Force Microscopy(AFM):
Tapping mode AFM measurements under ambient conditions were performed on Nanoscope III microscope (Digital Instruments).

S2. DLS characterization of the ssDNA/micelle complex:

Complexation happened upon mixng the ssDNA chains with PEO_{71}-$QP2VP_{12}$-PS_{29} micelles in water, due to the interaction between the negatively charged ssDNA and the positively charged QP2VP inner shell of the micelles. The complexation led to a slightly increased $\langle R_h \rangle$ (12 nm) measured immediately (~2 min) after the mixing (Fig. S1b). TEM observation made immediately after the mixing (Fig. 1a in the main text) indicates that the complex formed at very beginning of the complexation was with toroidal morphology, which should result from the complexation between one DNA chain and one micelle (see the discussion in the main text). DLS measurements

demonstrated that, 10 min and 24 h after mixing <Rh> exhibited a further increase to ~100 nm (Fig. S1c) and ~300 nm (Fig. S1d), respectively. The DLS results indicated that secondary aggregation of the ssDNA/micelle complex took place.

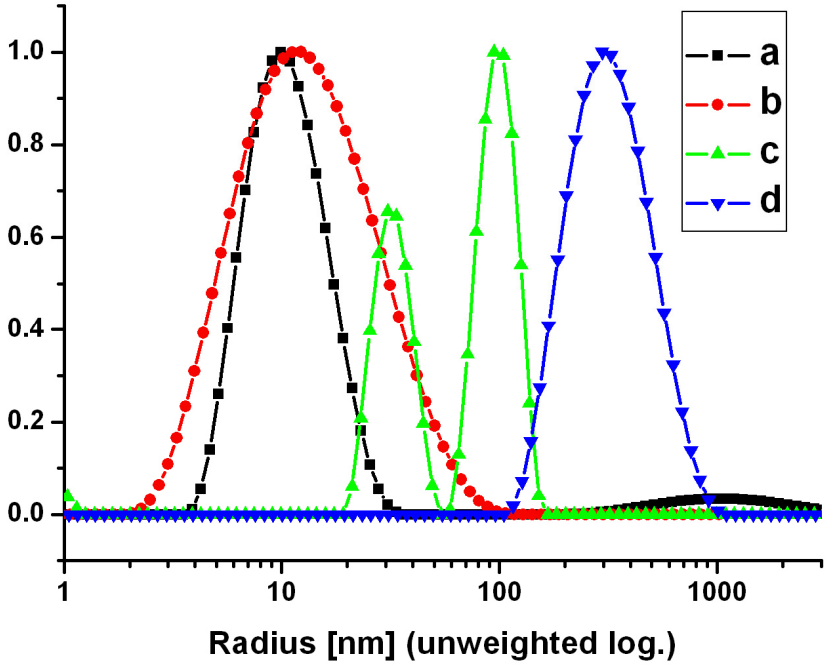

Fig. S1 DLS curves of: a: PEO-QP2VP-PS micelles, b: ssDNA/micelle complex measured immediately (~2 min) after mixing ssDNA with the micelles; c: ssDNA/micelle complex measured 10 min after the mixing and d: ssDNA/micelle complex measured 24 hours after the mixing.

S3. TEM images of FSFs obtained in different repeated experiments:

FSFs can be repeatedly prepared from self-assembly of the ssDNA/micelle complex. As described, the specimens for TEM observations were dried under vacuum at -60 ℃ for 72 hours. Besides, in the TEM images, some FSFs are overlapped and corrugations can be seen in FSFs. These confirm that FSFs were formed in solution.

Fig. S2a, b and c were unstained. We can see contrast in the structure (a network structure). However, in Fig. S2d, which is stained by RuO_4, no such contrast can be seen. This demonstrates that areas with a relatively low contrast in TEM images of the unstained FSFs are not empty but filled with the PEO and the PS components. These two components are invisible under TEM observations without staining but visible after being stained by RuO_4. This is consistent with the AFM results that the surface of FSFs is rather smooth.

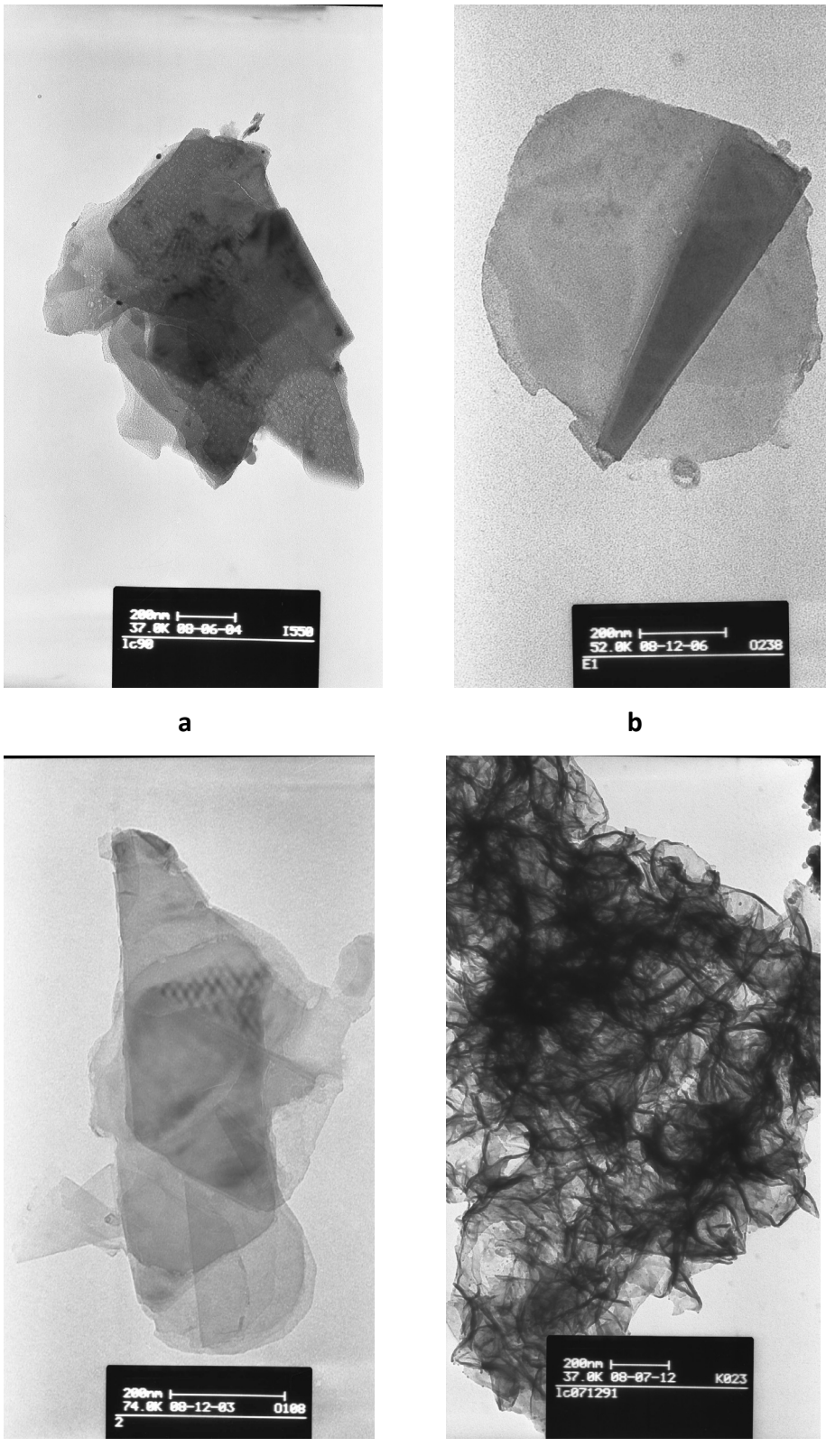

Fig. S2 TEM images of the FSFs obtained from the two-dimensional self-assembly of the ssDNA/micelle complex. The FSFs in TEM images of a, b, and c were unstained. The FSF in TEM image d was stained by RuO_4.

S4. TEM observation of the toroidal ssDNA/micelle complex after the

staining with RuO_4

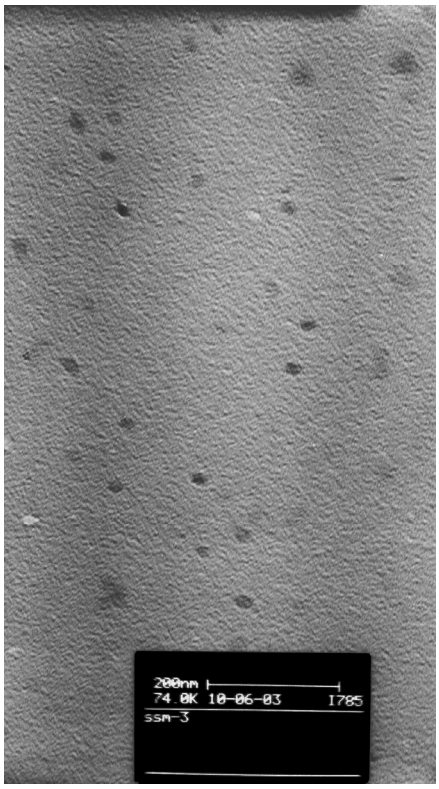

Fig. S3 TEM image of the toroidal ssDNA/micelle complex after the staining with RuO_4. The central area of the toroidal aggregates is not hollow. After the staining, the contrast of the PEO and PS components increase, so that no difference between the peripheral and the central area can be seen. This confirms the conclusion that the toroidal aggregates are not hollow but filled with the PEO and PS components.