Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Supramolecular Nanofibers *via* Protrusion Budding Interfacial Membrane

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Experimental section

Materials

Two triblock terpolymers of polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PS_{13k}-*b*-$P2VP_{9k}$-*b*-$PEO_{10.5k}$ and PS_{45k}-*b*-$P2VP_{38k}$-*b*-PEO_{58k}) were purchased from “Polymer Source” with a narrow PDI of 1.15. Deionized water, ethanol (Mreda, 99.7%) and cyclohexane (Damas-Beta, 99.9%) were purified with PTFE filter (pore size 100 nm). RuO_2 (Alfa-Aesar, 98%), $NaIO_4$ (Damas-Beta, 98%), iodine (Heowns, 99%) and phosphotungstic acid (Macklin, 99%) were used as staining agents as received.

Formation of the Nanofibers

After the example terpolymer of PS_{13k}-*b*-$P2VP_{9k}$-*b*-$PEO_{10.5k}$ was dispersed in water under sonication for 5 min, a desired amount of cyclohexane was fed to form the oil/water emulsion at 50 °C (above Θ temperature of polystyrene[1] and below the cloud point temperature of polyethylene oxide[2]) under stirring at 300 rpm. The emulsion was exposed to allow evaporation of the solvent to grow the nanofibers under stirring at 30 °C. The dispersions were sampled at varied time and immediately cryo-dried for TEM imaging.

In the fabrication of composite nanofibers with nanoparticles (Au NP or Fe_3O_4 NP) encapsulated, the same protocol was applied with the exception that the cyclohexane phase contained oleylamine (OAM) capped Au NP (*ca.* 4 nm, 10 mg/mL) or Fe_3O_4 NP (*ca.* 15 nm, 2 mg/mL), which were synthesized according to previous report.[3]

Characterization

TEM images were recorded on JEM-1011 (JEOL) at an accelerating voltage of 100 kV. The selective staining of PEO layer of the nanofibers was performed in the dispersion by feeding phosphor tungstate acid (40% of PEO) prior to the sample preparation for TEM observation. The selective staining of PVP block of the nanofibers with iodine vapor was performed on the cryo-dried samples in an iodine flask for 20 min. SEM images were recorded on JSM 7900F (JEOL) at an accelerating voltage of 15 kV. Residual amount of cyclohexane during the evaporation was determined by GC-FID (gas chromatograph with flame ionization detector, Trace1300, Thermo) with a 30 m × 0.32 mm × 1µm column (DB-WAXETR, Agilent, J&W Scientific).

Precipitates of PS_{13k}-*b*-$P2VP_{9k}$-*b*-$PEO_{10.5k}$ in water and cyclohexane, SEM images of the cyclohexane droplets stabilized with the BCP after drying, evaporation dependence of cyclohexane on temperature from the BCP, TEM images of self-assembled PS_{45k}-*b*-$P2VP_{38k}$-*b*-PEO_{58k}.

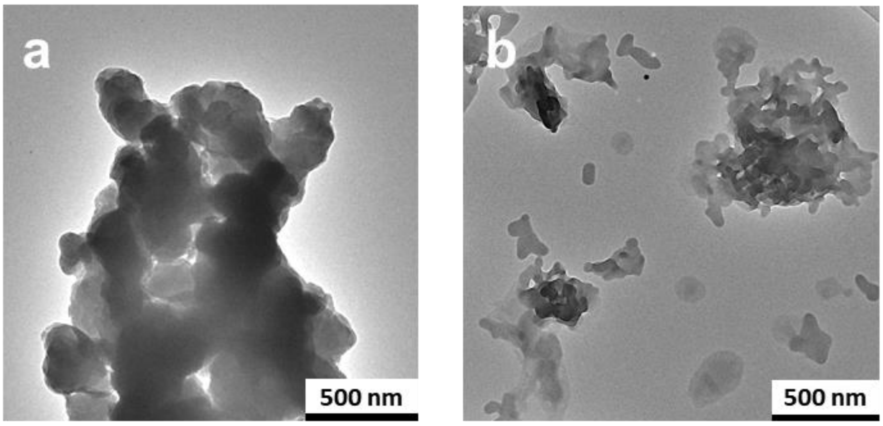

Figure S1. Precipitates of PS_{13k}-*b*-$P2VP_{9k}$-*b*-$PEO_{10.5k}$ in: (a) water; (b) cyclohexane. The concentration is fixed at 1 mg/mL.

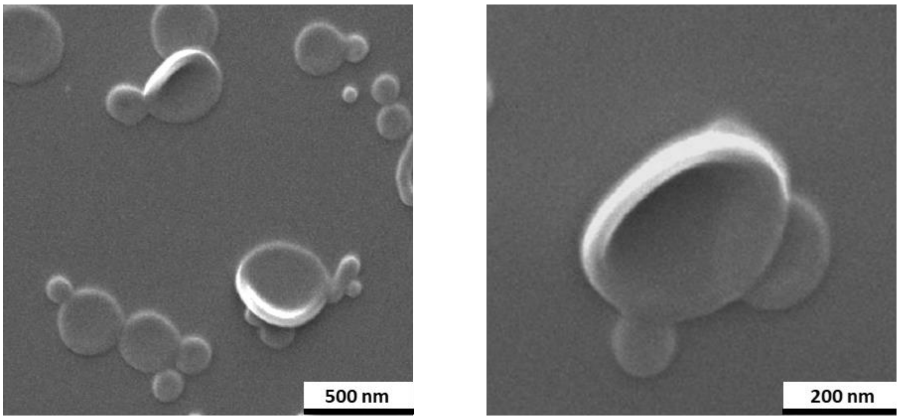

Figure S2. SEM images of the cyclohexane droplets stabilized with the terpolymer after cryo-drying. Both collapsed pie-like and bowl-like micelles are present.

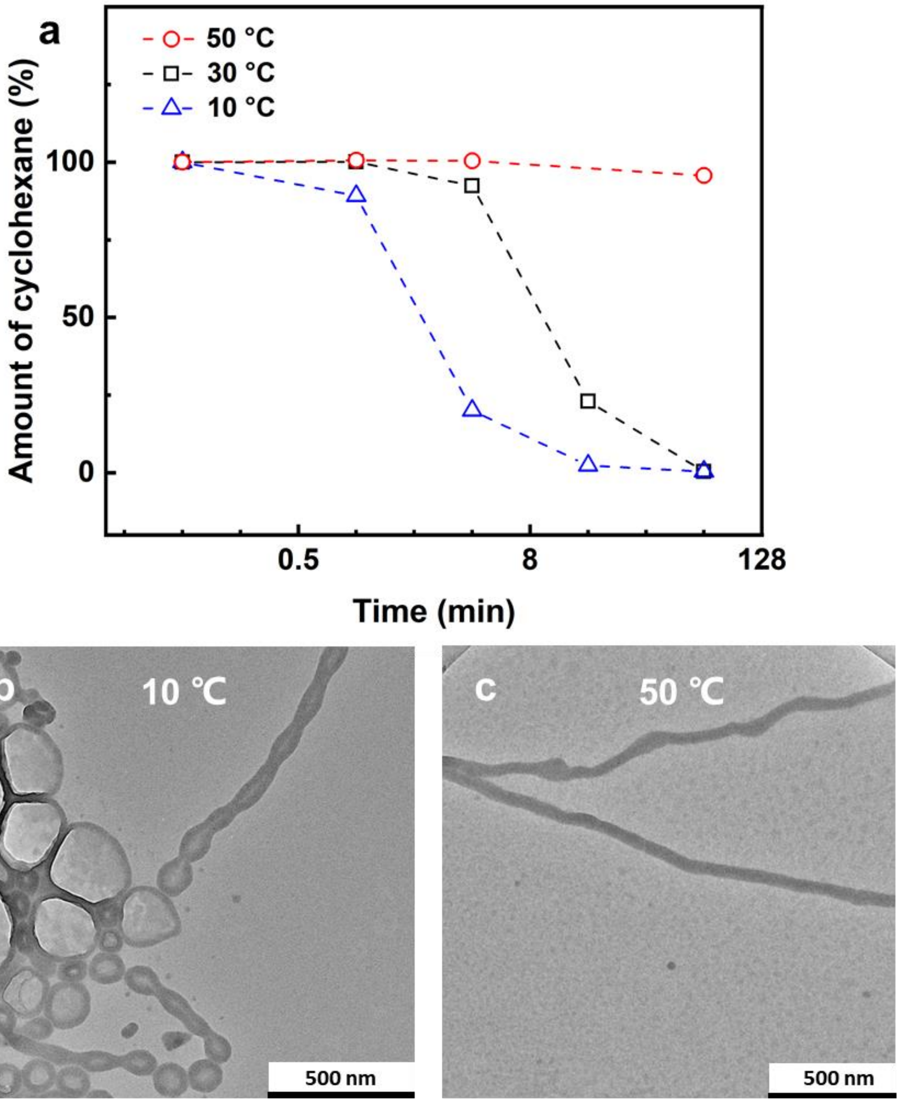

Figure S3. (a) Evaporation dependence of cyclohexane on temperature from the PS$_{13k}$-*b*-P2VP$_{9k}$-*b*-PEO$_{10.5k}$ (1 mg/mL) stabilized emulsion. (b, c) The assembled morphologies at 10 °C and 50 °C after stirring for 2 h.

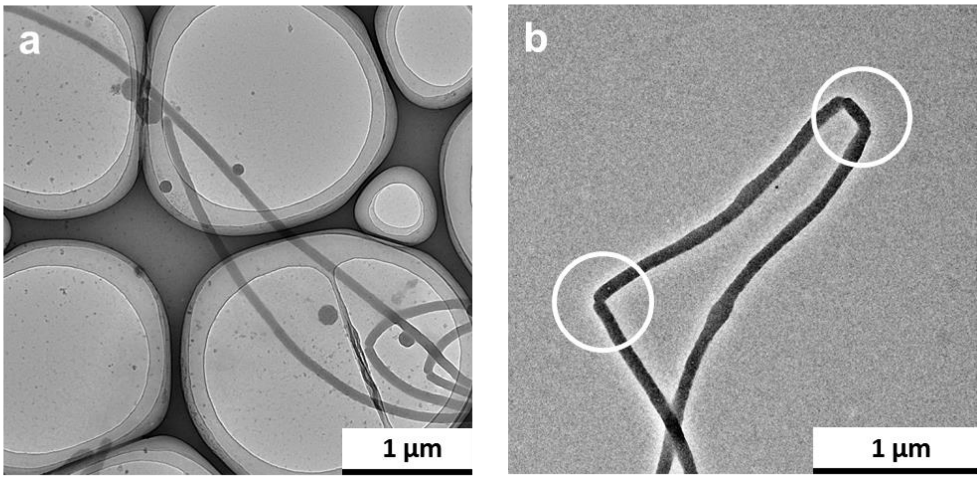

Figure S4. The self-assembled morphology of (a) PS_{45k}-*b*-$P2VP_{38k}$-*b*-PEO_{58k} (1 mg/mL); (b) the magnified TEM image.

1. S. Saeki, N. Kuwahara, S. Konno and M. Kaneko, *Macromolecules*, 1973, **6**, 246-250.
2. E. Florin, R. Kjellander and J. C. Eriksson, *J. Chem. Soc., Faraday trans. 1*, 1984, **80**, 2889-2910.
3. B. H. Wu, H. Y. Yang, H. Q. Huang, G. X. Chen and N. F. Zheng, *Chin. Chem. Lett.*, 2013, **24**, 457-462.