Electronic Supplementary Material (ESI) for Polymer Chemistry.

Self-Assembly of Single-Chain Nanoparticles from Block Copolymers into Inverse Bicontinuous Structures

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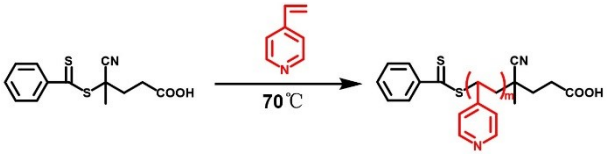
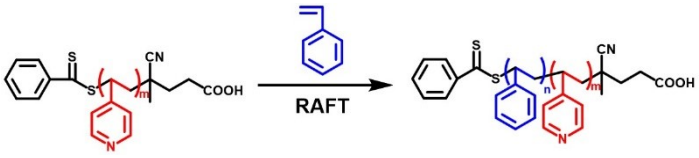
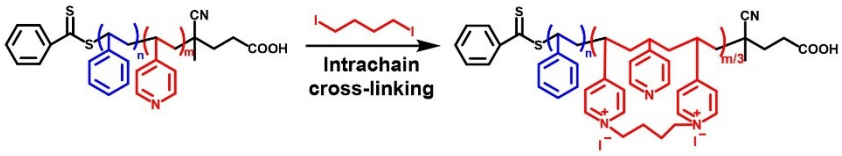
Synthesis routes of P4VP-CTA, P4VP-*b*-PS, and P4VP(SCNP)-*b*-PS



Scheme S1. The synthesis route of P4VP-CTA.



Scheme S2. The synthesis route of P4VP-*b*-PS.



Scheme S3. The synthesis route of P4VP(SCNP)-*b*-PS.

Characterization.

NMR Spectroscopy. ^{1}H NMR spectra were obtained by Bruker DMX Spectrometer (400 MHz) using $CDCl_3$ as a solvent.

Gel Permeation Chromatography (GPC). The P4VP-*b*-PS and P4VP(SCNP)-*b*-PS were measured on Waters 2410 GPC. The eluent was THF with a flow rate of 1 mL/min. The samples were dissolved in THF, and filtered through 0.22 μm syringe filters. The calibration curves were obtained from PS standards. Some samples were also measured on a system comsisted of Wyatt Technology detector, Agilent HPLC pump, and Agilent mixed columns (Plgel 20 μm MIXED-A and PLgel 10 μm MIXED-B). The eluent of DMF with LiBr (0.05 mol/L) was used and the measurements were conducted at 25 °C with a flow rate of 1 mL/min.

Dynamic Light Scattering (DLS). DLS measurements were conducted on the instrument of Shandong Naikete NKT-N9 with a 532 nm He-Ne laser.

Scanning Electron Microscopy (SEM). Images were taken using a Tescan Vega3 microscope with an accelerating voltage of 30 kV and a Zeiss SUPRA55 instrument at an accelerating voltage of 10

kV. The dilute dispersion solution was dropped onto a silicon wafer and then sputtered with gold.

Transmission Electron Microscopy (TEM). Images were taken using a JEM-2100Plus microscope with an accelerating voltage of 200 kV. The dilute dispersion solution was dropped onto a copper grid.

Small Angle X-ray Scattering (SAXS). SAXS measurements were performed on the synchrotron radiation at BL16B1 beamline provided by Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 1.24 Å at room temperature.

Synthesis of P4VP-CTA via RAFT solution polymerization

P4VP macromolecular chain transfer agents (macro-CTAs) were synthesized by reversible addition-fragmentation chain transfer (RAFT) solution polymerization (Scheme S1). Typically, 4-VP (0.63 g, 6.0 mmol), CPADB (40.5 mg, 0.1 mmol), and AIBN (1.64 mg, 0.01 mmol) dissolved in 3 mL ethanol were added into a Schlenk flask. After three freeze-pump-thaw cycles, the flask was sealed. The reaction was quenched in liquid nitrogen after 6 h at 70 °C and precipitated in petroleum ether three times. Then the product was dialyzed in ethanol and dried under vacuum. The degree of polymerization of P4VP (DP_{P4VP}) is calculated by ^{1}H NMR (Figure S1) as follows:

$$DP_{P4VP} = \frac{I_d}{I_b} \quad \text{(S1)}$$

where I_b represents the integrated value of the proton peaks originating from the phenyl groups of 4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB) (signal b, δ = 7.78-7.90 ppm); I_d represents the integrated value of the proton peaks attributed to the pyridine groups of P4VP block (signal d, δ = 8.15-8.65 ppm).

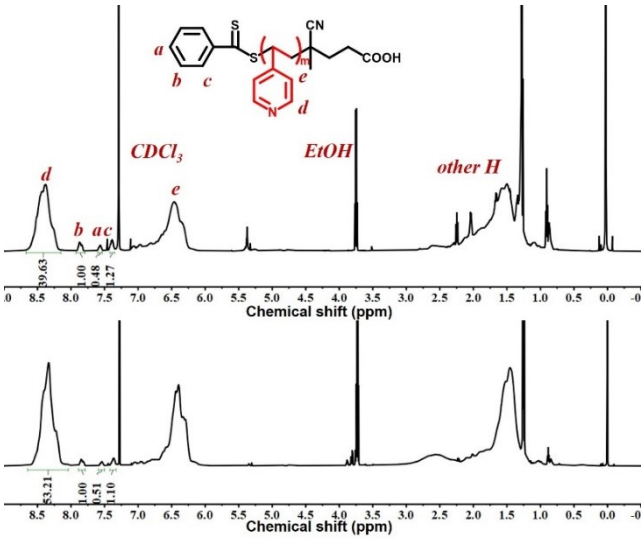


Figure S1 ^{1}H NMR spectra of $P4VP_{40}$-CTA and $P4VP_{53}$-CTA (from top to bottom).

Synthesis of P4VP-*b*-PS via RAFT dispersion polymerization

The degree of polymerization of PS (DP_{PS}) is calculated by ^{1}H NMR as follows:[1]

$$\frac{I_{a}}{I_{b+c+d}} = \frac{2 \times DP_{P4VP}}{5 \times DP_{PS} + 2 \times DP_{P4VP}} \quad \text{(S2)}$$

where I_a represents the integrated value of the proton peaks at 8.20-8.60 ppm, originating from the pyridine groups of P4VP block (signal a); I_{b+c+d} represents the integrated value of the proton peaks at 6.20-7.20 ppm, originating from the phenyl groups of PS block and the pyridine groups of P4VP block. Accordingly, the DP_{PS} is calculated as follows:

$$DP_{PS} = \frac{2 \times DP_{P4VP} \times \left(\frac{I_{b+c+d+e}}{I_{a}} - 1 \right)}{5} \quad \text{(S3)}$$

Taking $P4VP_{53}$-*b*-PS_{499} as an example:

$$DP_{PS} = \frac{2 \times DP_{P4VP} \times (\frac{I_{b+c+d+e}}{I_{a}} - 1)}{5} = \frac{2 \times 53 \times (\frac{24.56}{1} - 1)}{5} \approx 499$$

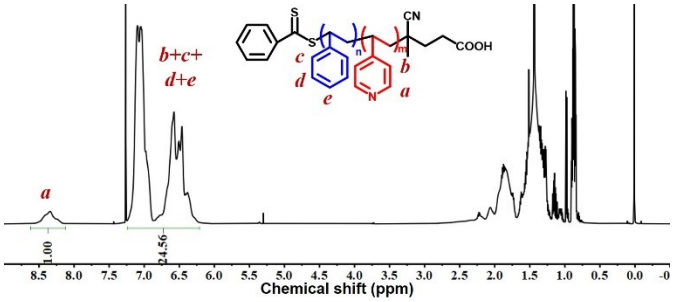


Figure S2. ^{1}H NMR spectrum of P4VP$_{53}$-*b*-PS$_{499}$.

The volume fraction of the PS block (f_{PS}) is calculated as follows:[2]

$$f_{PS} = \frac{V_{PS}}{V_{P4VP} + V_{PS}} = \frac{M_{PS}/\rho_{PS}}{M_{P4VP}/\rho_{P4VP} + M_{PS}/\rho_{PS}} \quad \text{(S4)}$$

In equation S4, V_{P4VP} and V_{PS} represent the volumes of P4VP and PS chains respectively; M_{P4VP} and M_{PS} denote the molecular weights of the P4VP and PS blocks, respectively; ρ_{P4VP} represents the density of P4VP, which is about 1.15 g cm^{-3}; ρ_{PS} represents the density of PS, which is about 1.05 g cm^{-3}.

Taking P4VP$_{53}$-*b*-PS$_{499}$ as an example:

$$f_{PS} = \frac{V_{PS}}{V_{P4VP} + V_{PS}} = \frac{M_{PS}/\rho_{PS}}{M_{P4VP}/\rho_{P4VP} + M_{PS}/\rho_{PS}} = \frac{499 \times 104/1.05}{53 \times 105/1.15 + 499 \times 104/1.05} \approx 91.1\%$$

Preparation and characterization of tadpole-like SCNPs.

The number of DIB (x) linked to P4VP is calculated by ^{1}H NMR as follows:

$$x = \frac{1}{4} \times \frac{I_f \times 2 \times DP_{P4VP}}{I_a} \quad \text{(S5)}$$

Therefore, the actual CD of SCNPs is calculated by the following equation:

$$\text{CD} = \frac{2x}{\text{DP}_{\text{P4VP}}} \times 100\% = \frac{I_f}{I_a} \times 100\% \quad \text{(S6)}$$

Taking CD$_{27\%}$-P4VP(SCNP)$_{53}$-*b*-PS$_{569}$as an example (Figure S3):

$$x = \frac{1}{4} \times \frac{I_f \times 2 \times \text{DP}_{\text{P4VP}}}{I_a} = \frac{1}{4} \times \frac{0.27 \times 2 \times 53}{1} = 7.155$$

$$\mathrm{CD} = \frac{2 \times 7.155}{53} \times 100\% = \frac{I_f}{I_a} \times 100\% = \frac{0.27}{1} \times 100\% = 27\%$$

So, this sample can be named $CD_{27\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569}.

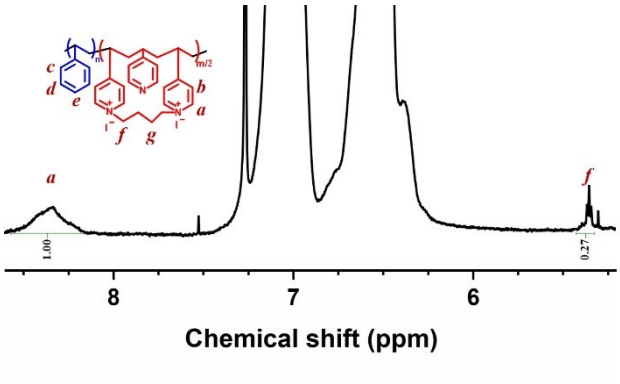


Figure S3. ^{1}H NMR spectrum of $CD_{27\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569} prepared in dilute DCM solution.

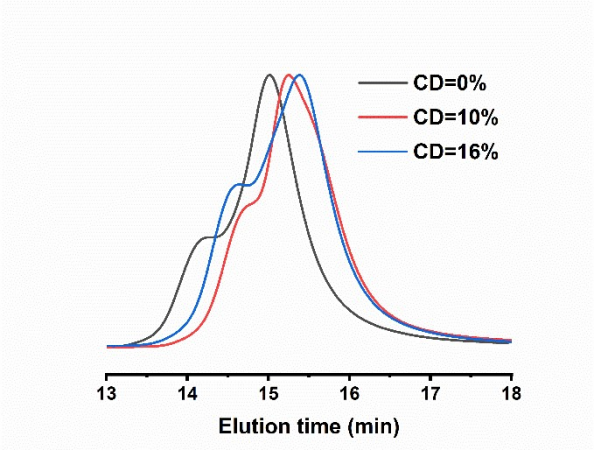


Figure S4. GPC traces of P4VP(SCNP)$_{40}$-*b*-PS_{512} using DMF as the eluent.

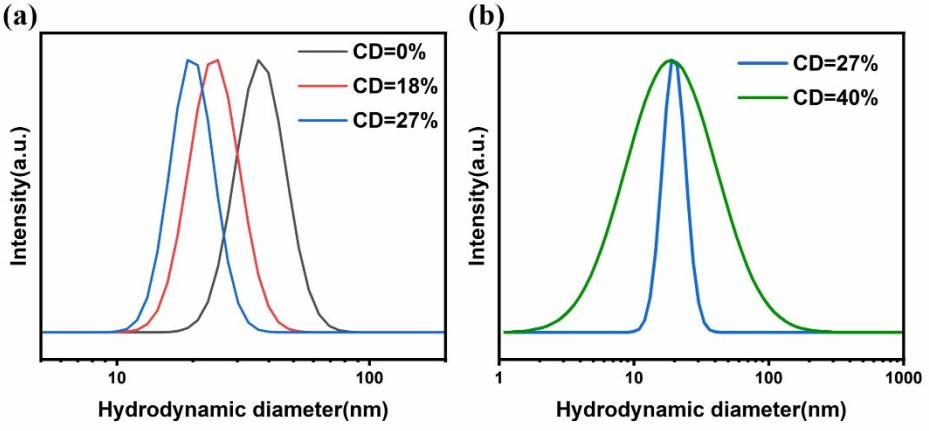


Figure S5. (a) DLS curves of P4VP$_{53}$-*b*-PS_{569} and P4VP(SCNP)$_{53}$-*b*-PS_{569} at CD of 0%, 18%, and 27%.

(b) Comparison curves between 27% and 40%.

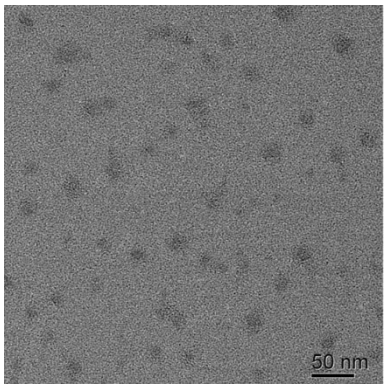


Figure S6. TEM image of tadpole-like SCNPs ($CD_{27\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569}) prepared in dilute DCM solution.

Self-assembly behavior of linear BCPs and tadpole-like SCNPs in solution.

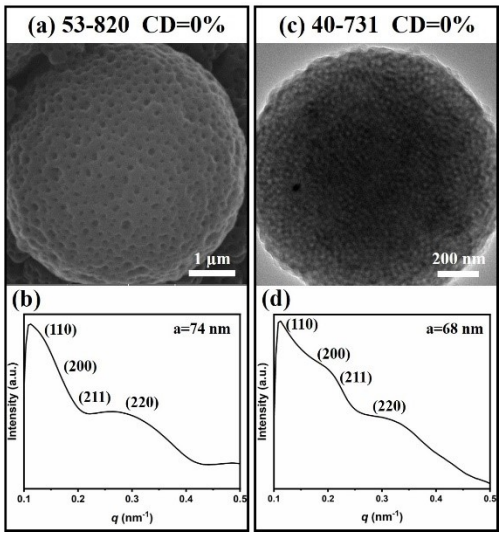


Figure S7. Cubosomes obtained by linear P4VP-*b*-PS using DMF as co-solvent. (a, b) SEM image and SAXS pattern of $P4VP_{53}$-*b*-PS_{820} (f_{PS}=94.4%) ; (c,d) TEM image and SAXS pattern of $P4VP_{40}$-*b*-PS_{731} (f_{PS}=95.2%).

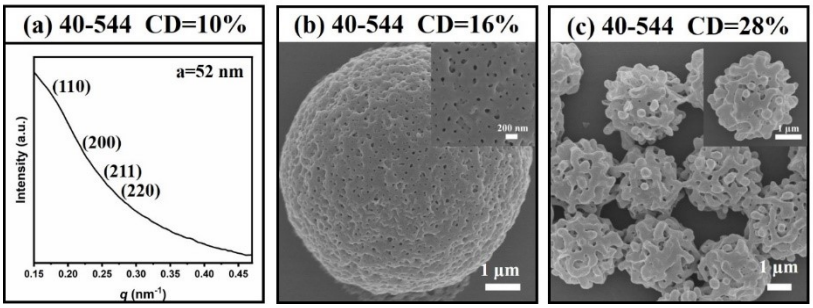


Figure S8. (a) SAXS profile of cubosomes formed by $CD_{10\%}$-P4VP(SCNP)$_{40}$-*b*-PS_{544}. SEM images of (b) irregular cubosomes formed by $CD_{16\%}$-P4VP(SCNP)$_{40}$-*b*-PS_{544} and (c) LCMs formed by $CD_{28\%}$-P4VP(SCNP)$_{40}$-*b*-PS_{544} using DMF as co-solvent.

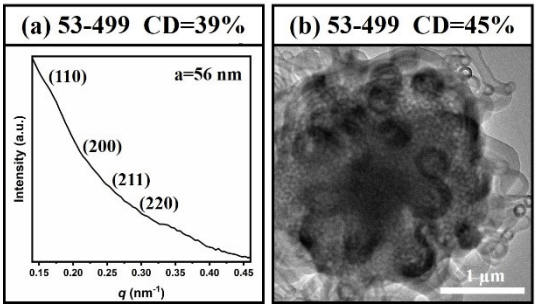


Figure S9. (a) SAXS profile of cubosomes formed by $CD_{39\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{499} and (b) TEM image of LCMs with irregular pores and elongated vesicles formed by $CD_{45\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{499} using DMF as co-solvent.

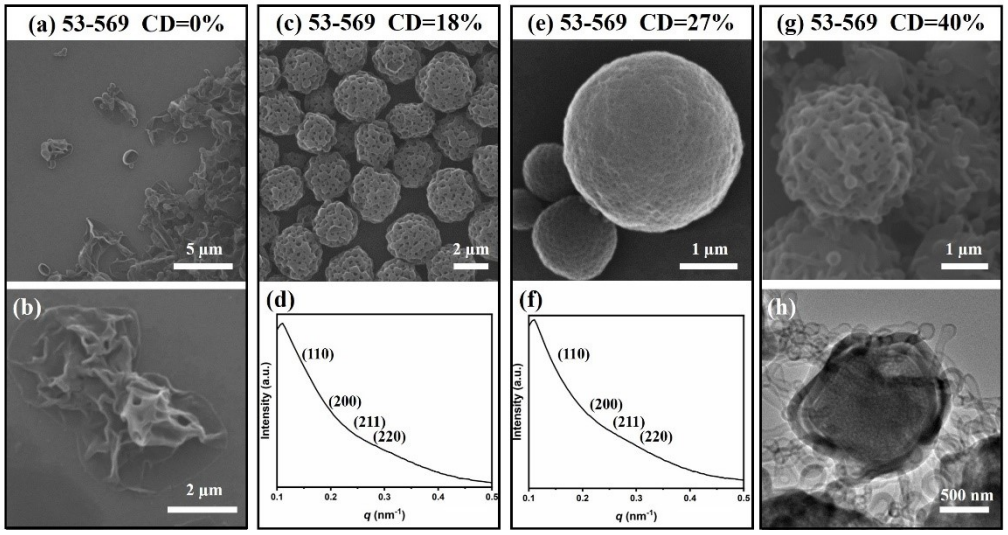


Figure S10. (a, b) SEM images of LCVs formed by linear P4VP$_{53}$-*b*-PS_{569}; (c, e) SEM images and (d, f) SAXS patterns of cubosomes formed by $CD_{18\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569} and $CD_{27\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569}, respectively; (g) SEM image and (h) TEM image of cubosomes with uneven surface formed by $CD_{40\%}$-P4VP(SCNP)$_{53}$-*b*-PS_{569}. All the self-assembles were obtained by using DMF as co-solvent.

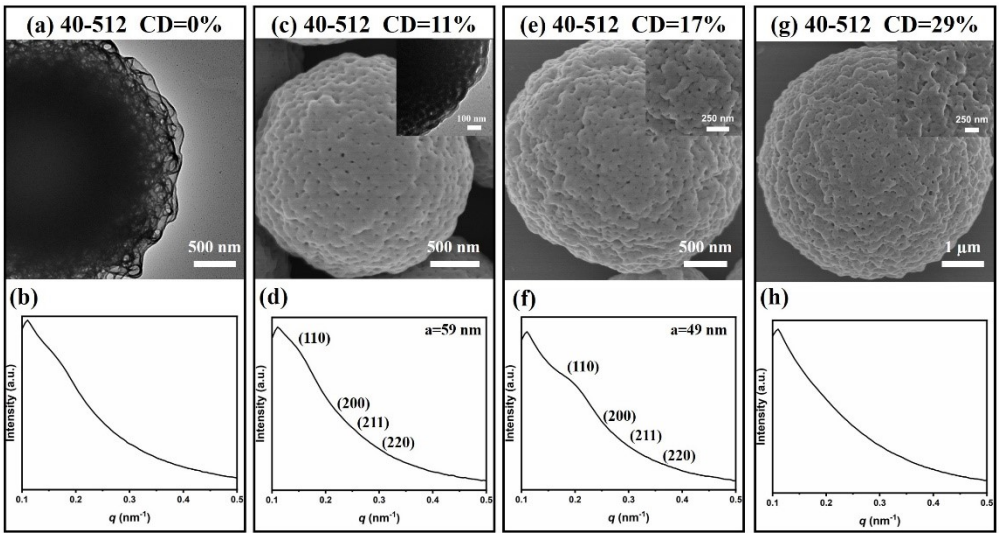


Figure S11. (a) TEM image and (b) SAXS pattern of sponges formed by linear $P4VP_{40}$-*b*-PS_{512}; (c, e) SEM images (inserts were TEM and SEM image at magnification) and (d, f) SAXS patterns of cubosomes formed by $CD_{11\%}$-$P4VP(SCNP)_{40}$-*b*-PS_{512} and $CD_{17\%}$-$P4VP(SCNP)_{40}$-*b*-PS_{512}, respectively; (g) SEM images and (h) SAXS pattern of LCMs formed by $CD_{29\%}$-$P4VP(SCNP)_{40}$-*b*-PS_{512}. All the self-assembles were obtained by using DMF as co-solvent.

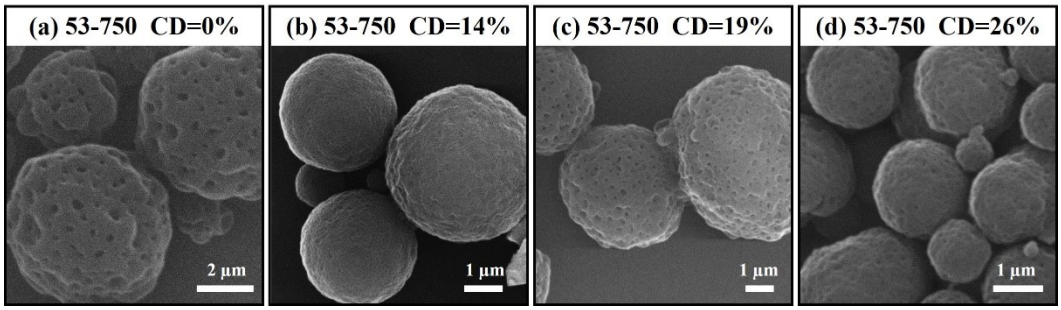


Figure S12. SEM images of (a) sponges obtained by linear $P4VP_{53}$-*b*-PS_{750}, cubosomes obtained by (b) $CD_{14\%}$-$P4VP(SCNP)_{53}$-*b*-PS_{750} and (c) $CD_{19\%}$-$P4VP(SCNP)_{53}$-*b*-PS_{750}, and (d) LCMs obtained by $CD_{26\%}$-$P4VP(SCNP)_{53}$-*b*-PS_{750} using DMF as co-solvent.

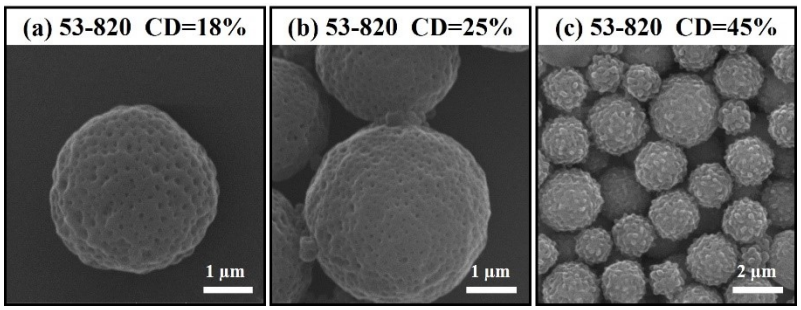


Figure S13. SEM images of cubosomes formed by (a) $CD_{18\%}$-$P4VP(SCNP)_{53}$-*b*-PS_{820} and (b) $CD_{25\%}$-

P4VP(SCNP)$_{53}$-*b*-PS$_{820}$, and (c) LCMs formed by CD$_{45\%}$-P4VP(SCNP)$_{53}$-*b*-PS$_{820}$ using DMF as co-solvent.

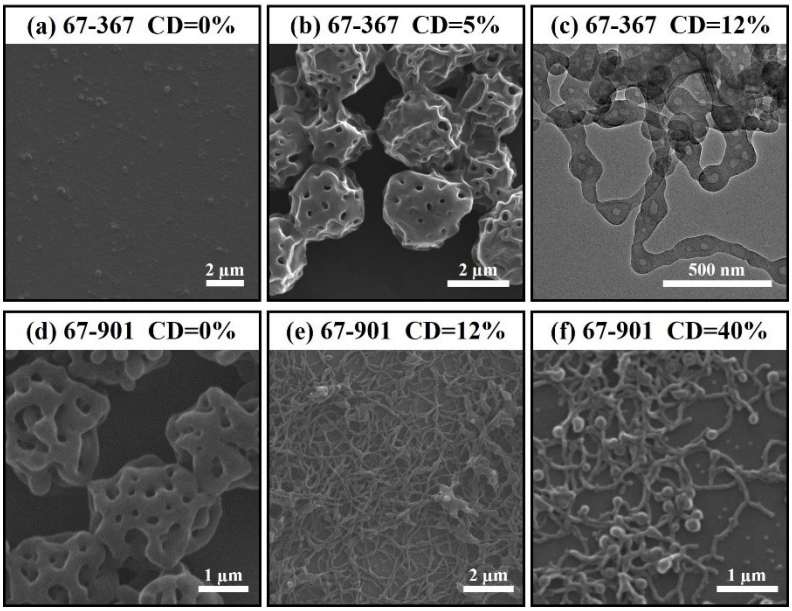


Figure S14. SEM images of (a) micelles formed by linear P4VP$_{67}$-*b*-PS$_{367}$, (b) sponges formed by CD$_{5\%}$-P4VP(SCNP)$_{67}$-*b*-PS$_{367}$, and (c) nanowires formed by CD$_{12\%}$-P4VP(SCNP)$_{67}$-*b*-PS$_{367}$ using DMF as co-solvent. SEM images of (d) sponges formed by linear P4VP$_{67}$-*b*-PS$_{901}$ and (e, f) nanowires formed by CD$_{12\%}$-P4VP(SCNP)$_{67}$-*b*-PS$_{901}$ and CD$_{40\%}$-P4VP(SCNP)$_{67}$-*b*-PS$_{901}$ using DMF as co-solvent.

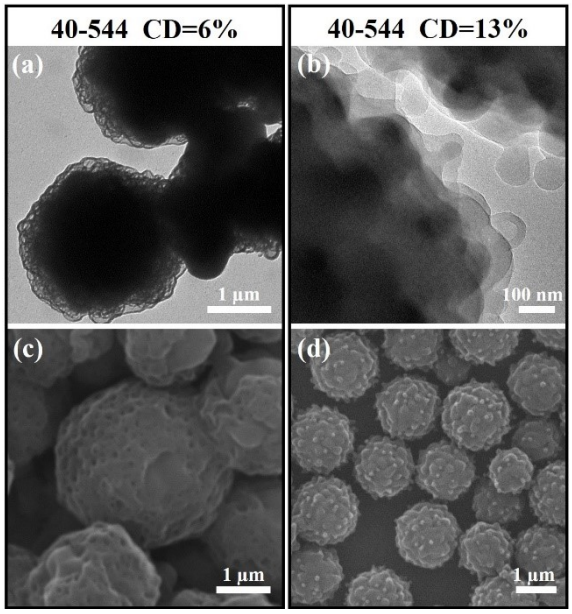


Figure S15. SEM and TEM images of (a, c) sponges formed by CD$_{6\%}$-P4VP(SCNP)$_{40}$-*b*-PS$_{544}$ and (b, d) LCMs with uneven surface formed by CD$_{13\%}$-P4VP(SCNP)$_{40}$-*b*-PS$_{544}$ using DMF as co-solvent. The

interchain cross-linking nanopartices were prepared in the dilute dioxane solution.

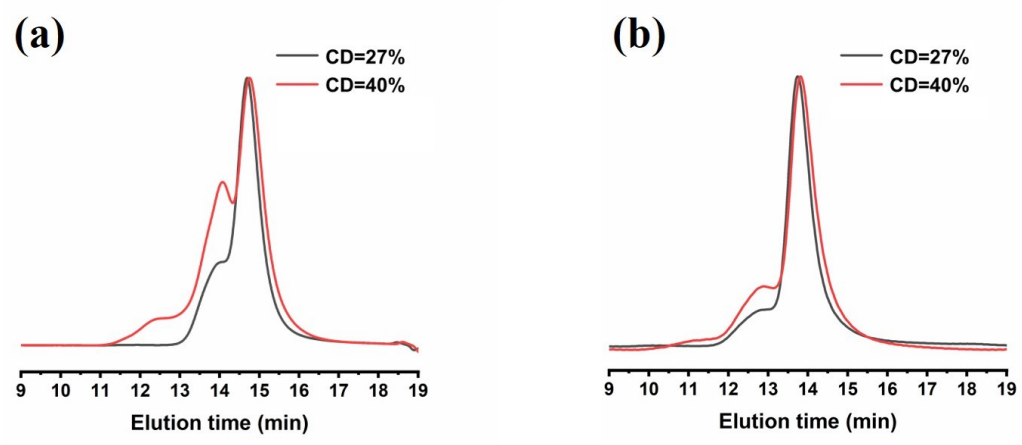


Figure S16. GPC traces of P4VP(SCNP)$_{53}$-*b*-PS$_{569}$ prepared in dilute DCM solution when CD was 27% and 40%, using (a) DMF and (b) THF as the eluent, respectively.

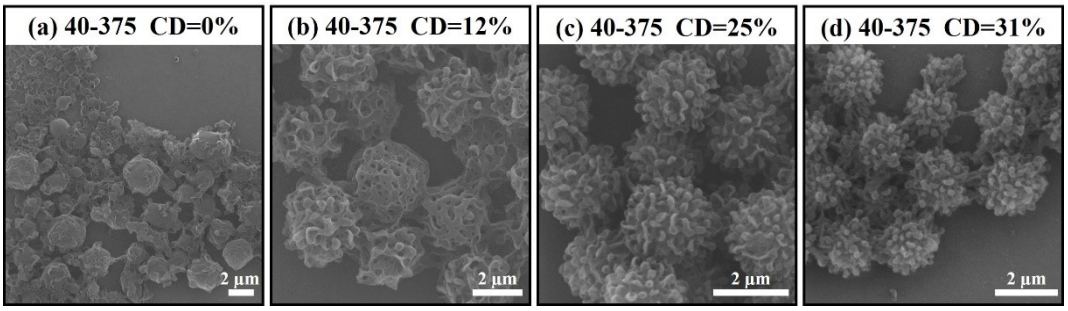


Figure S17. SEM images of (a) LCVs formed by linear P4VP$_{40}$-*b*-PS$_{375}$, (b) sponges formed by CD$_{12\%}$-P4VP(SCNP)$_{40}$-*b*-PS$_{375}$, and LCMs with uneven surface formed by (c) CD$_{25\%}$-P4VP(SCNP)$_{40}$-*b*-PS$_{375}$ and (d) CD$_{31\%}$-P4VP(SCNP)$_{40}$-*b*-PS$_{375}$ using DMF as co-solvent.

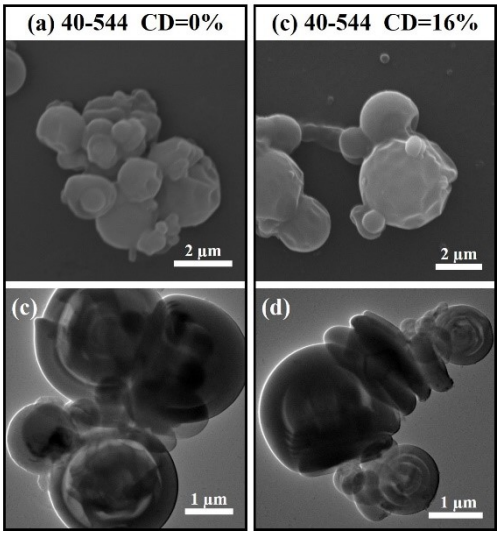


Figure S18. SEM and TEM images of LCVs formed by (a, b) linear $P4VP_{40}$-*b*-PS_{544} and (c, d) $CD_{16\%}$-$P4VP(SCNP)_{40}$-*b*-PS_{544} using THF as co-solvent.

Reference:

1.R. Liu, Z. Rong, G. Han, X. Yang and W. Zhang, *Polymer*, 2021, **215**, 123431.

2.Z. Lin, S. Liu, W. Mao, H. Tian, N. Wang, N. Zhang, F. Tian, L. Han, X. Feng and Y. Mai, *Angew. Chem., Int. Ed.*, 2017, **56**, 7135-7140.