

Electronic Supplementary Information for:

Cross-linked Reverse Micelles with Embedded Water Pools: A Novel Catalytic System Based on Amphiphilic Block Copolymers

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Characterization methods

The copolymer P4VP-PEG-P4VP was characterized by ¹H NMR and gel permeation chromatography (GPC). ¹H NMR spectroscopic analyses were performed using an Agilent DD2-600 NMR Spectrometers at 600 MHz. All spectra were recorded using DMSO-d₆ as the solvent and TMS as the external standard. The weight-average (M_w), number-average (M_n) molecular weights and molecular weight distributions (M_w/M_n) of the polymers were measured using a GPC equipped with an RI detector. The eluent was DMF with a flow rate at 1.0 mL/min. Polymer molecular weights were calibrated against polystyrene standards (Polymer Laboratories, Shropshire, UK).

Table S1. Comparison on structures of PEG-P4VP and P4VP-PEG-P4VP copolymers from ^1H NMR. and GPC^a measurements.

Copolymer	EG ^b	4VP ^b	M_n^b	M_n^c	PDI ^c
P4VP-PEG-P4VP	45	50	7200	7229	1.072

^a Polymer molecular weights were calibrated by polystyrene standards.

^b The calculated monomer repeat units from NMR.

^c Molecular weights and distributions from GPC traces.

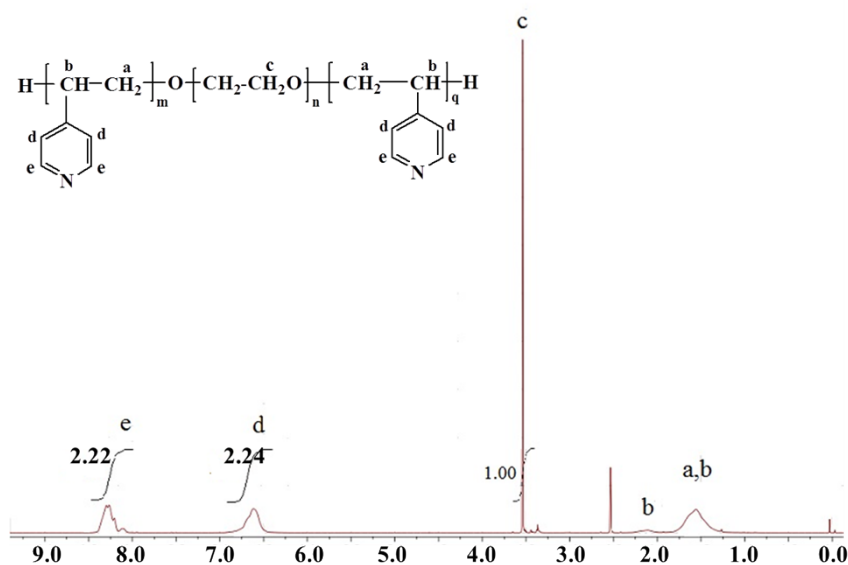


Figure S1. ^1H NMR spectrum of the synthesized P4VP-PEG-P4VP block copolymer in DMSO-d_6 .

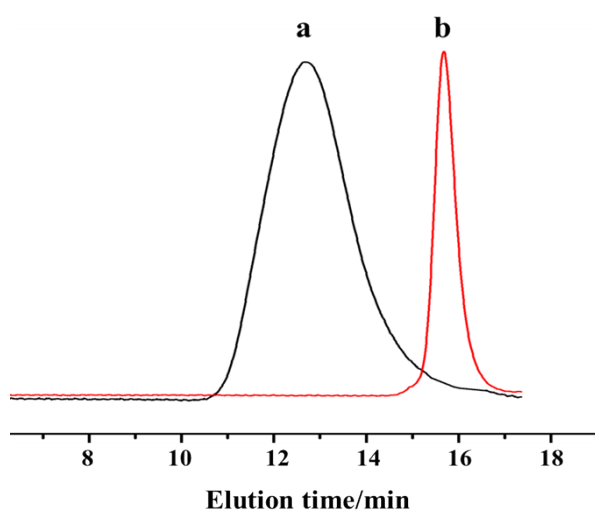


Figure S2. GPC traces of (a) P4VP-PEG-P4VP and (b) PEG ($M_n = 2000$) block copolymer in DMF.

The ^1H NMR spectrum of the final copolymer is shown in Figure S1. The sharp peak at 3.5 ppm is assigned to the methylene protons in the $-\text{CH}_2\text{CH}_2\text{O}-$ unit of the PEG block. The signals of $-\text{CH}_2$ and $-\text{CH}$ in the P4VP block overlap at 1.5 and 2.1 ppm¹⁻³. Those at 6.6 and 8.3 ppm can be assigned to the protons at the pyridine ring. The weak peak at 3.3 ppm is assigned to H_2O which is easily absorbed in DMSO-d_6 . The peak of DMSO-d_6 is at 2.5 ppm. In the ^1H NMR spectrum of P4VP-PEG-P4VP, the peaks at 3.5 ppm (H_c) and 8.3 ppm (H_e) can be used to calculate the number-average molecular weight and the block ratio of the copolymer⁴. The block ratio was calculated using the following equations:

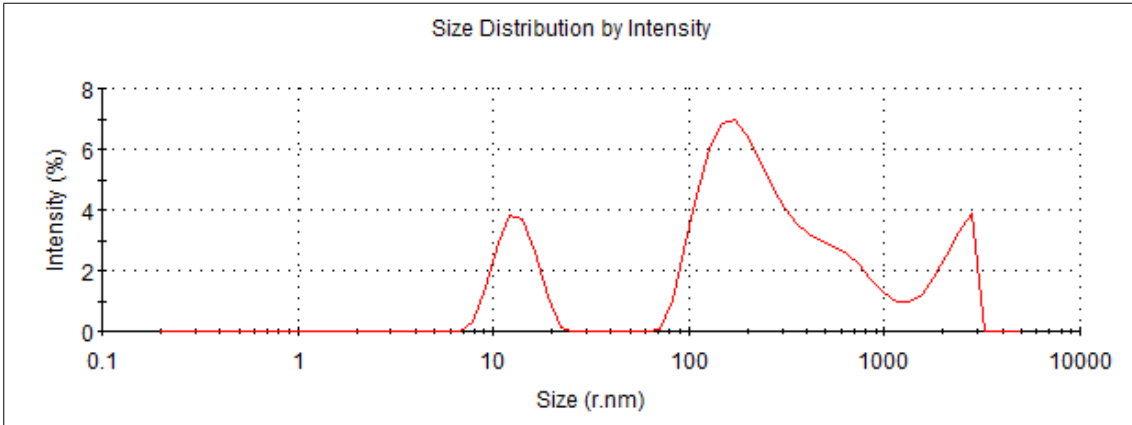
$$\frac{S_c}{S_e} = \frac{N_{\text{H}_c}}{N_{\text{H}_e}} = \frac{4n_{\text{PEG}}}{2n_{4\text{VP}}} = \frac{4 \times 2000/44}{2 \times n_{4\text{VP}}} \quad (1)$$

$$M_{\text{copolymer}} = 2000 + n_{4\text{VP}} \times M_{4\text{VP}} \quad (2)$$

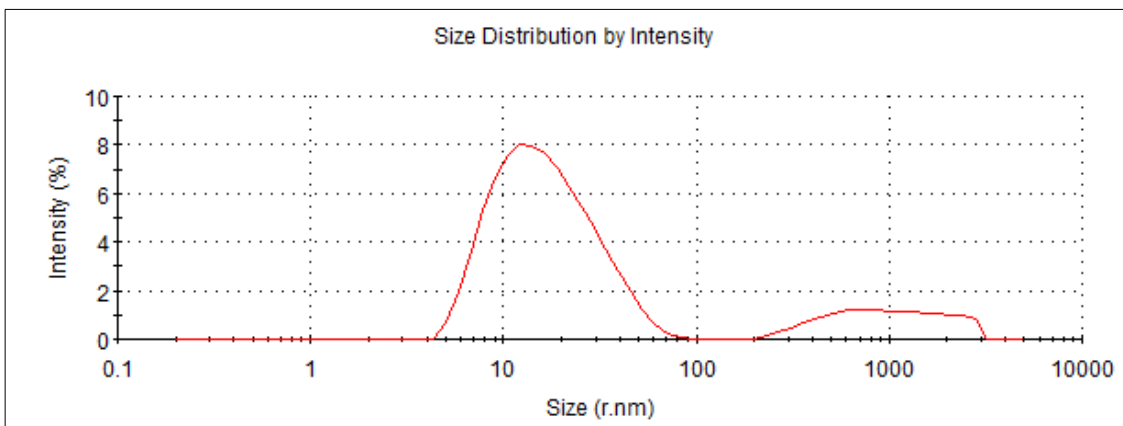
Where S is the intensity of peaks in the ^1H NMR spectrum; n_{PEG} and $n_{4\text{VP}}$ are the number of monomer repeat units along one copolymer backbone; $M_{\text{copolymer}}$ and $M_{4\text{VP}}$ are the number-molecular weights for the copolymer and 4VP respectively. Based on the calculation of the NMR spectrum, we found that one P4VP-PEG-P4VP chain had 45 EG units and 50 4VP units, with the $M_{\text{copolymer}}$ of 7200 g/mol.

The molecular weights and distributions of P4VP-PEG-P4VP and PEG from GPC traces were shown in Figure S2. PEG ($M_n = 2000$ g/mol) was the synthetic raw material for P4VP-PEG-P4VP (Figure S2b). The M_n values obtained from NMR and GPC measurements are consistent.

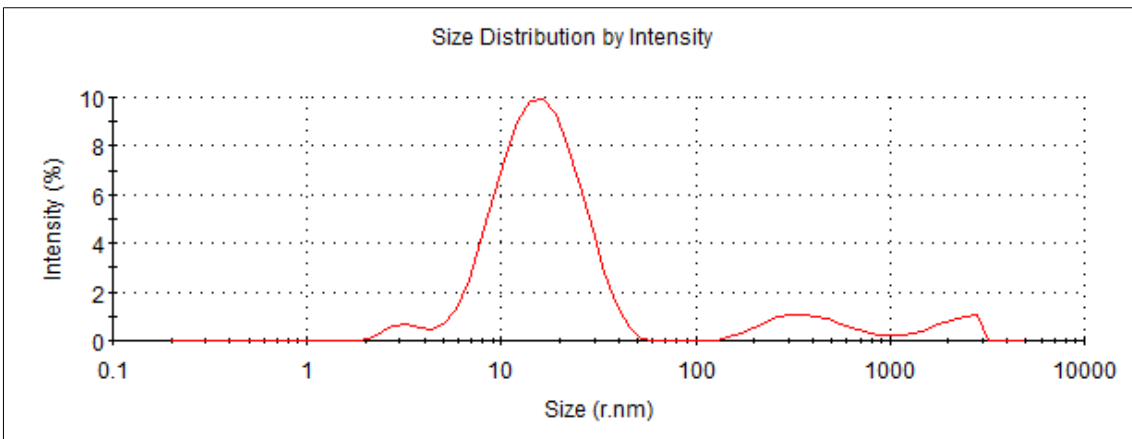
For comparison purpose, the PEG-P4VP diblock copolymer was also synthesized and characterized using same method. We could achieve the result that one PEG-P4VP chain has 45 EG units and 141 4VP units



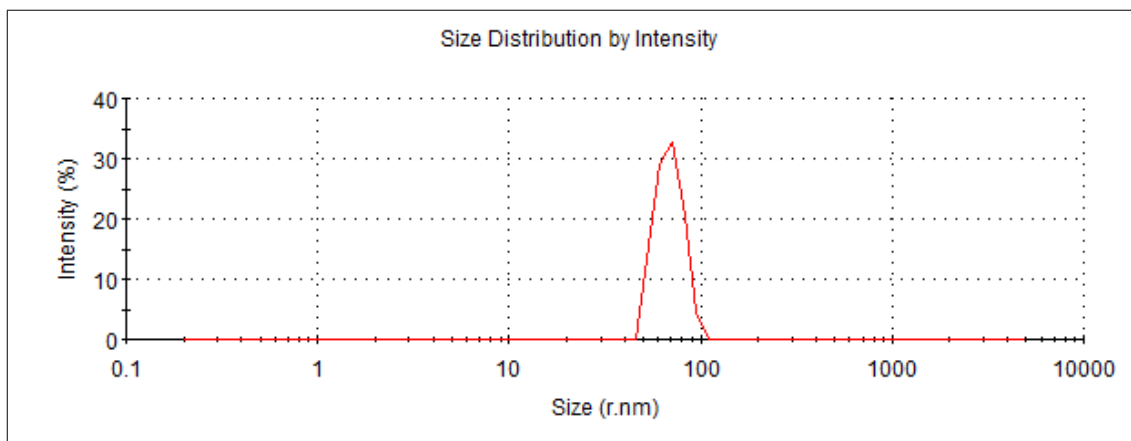
a)



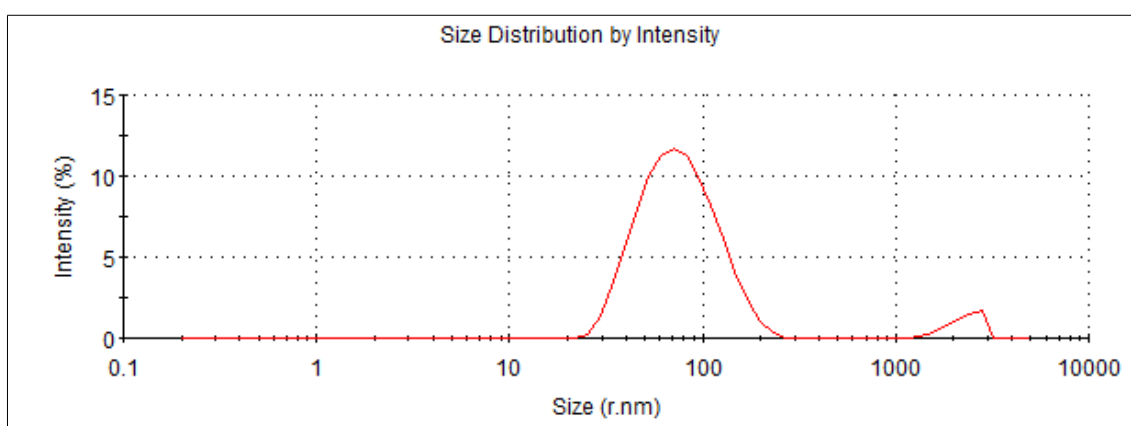
b)



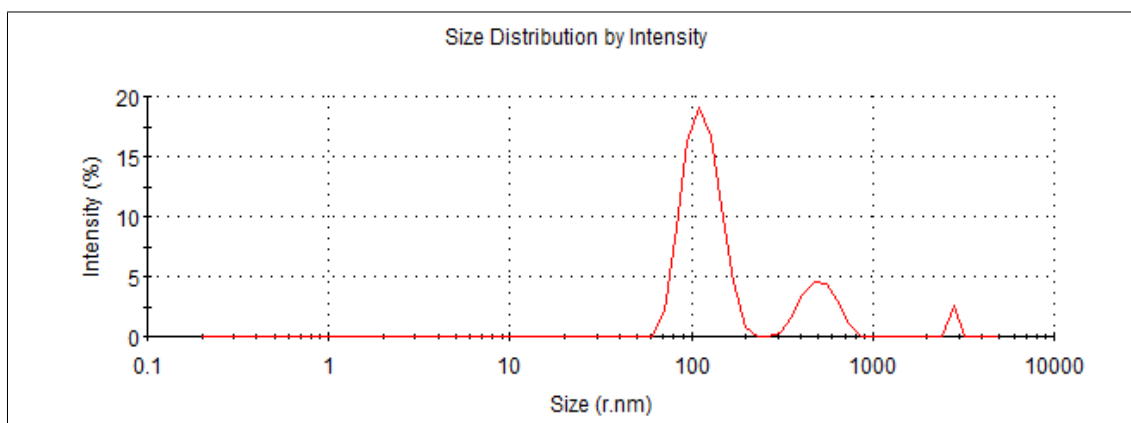
c)



d)



e)



f)

Figure S3. The particle size distribution of P4VP-PEG-P4VP self-assemblies at 25 °C prepared in a mixture solution of water/1-hexanol: a) 100% 1-hexanol, b) 80% 1-hexanol + 20% water, c) 60% 1-hexanol +40% water, d) 40% 1-hexanol + 60% water, e) 20% 1-hexanol + 80% water, f) 100% water. (polymer weight: 0.15 %)

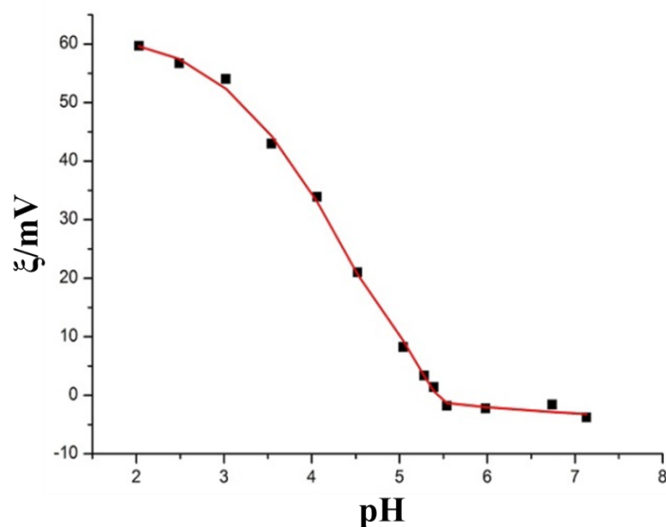


Figure S4. Plots of zeta potential versus pH of P4VP-PEG-P4VP reverse micelles in mixed solution (mass ratio of 1-hexanol/water = 1).

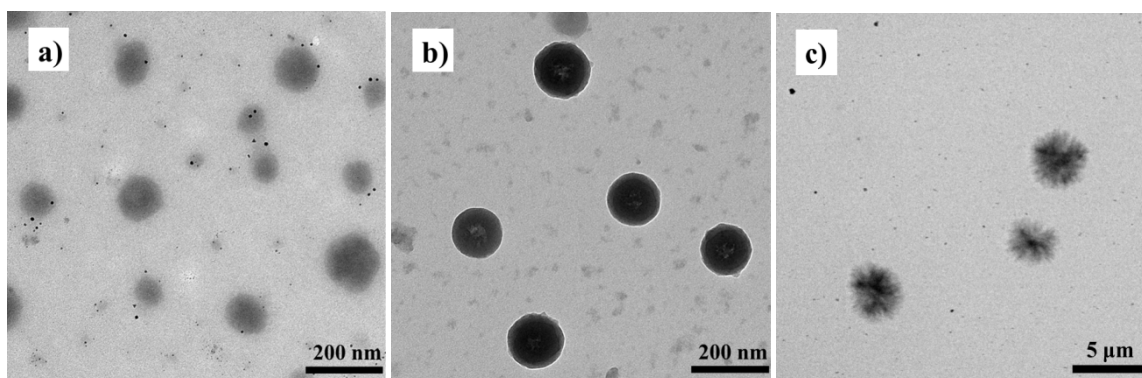


Figure S5. TEM images of P4VP-PEG-P4VP reverse micelles in mixed solution at different pH (polymer weight: 0.15 %, mass ratio of 1-hexanol/water = 1) : a) pH=2; b) pH=4; c) pH=6.

In Figure S4, the plots showed the potential versus pH for the P4VP-PEG-P4VP RMs. With the increase of pH, the degree of protonation of P4VP decreased, and thus the potential decreased⁵. The 4VP units were protonated at pH 4, and therefore the P4VP-PEG-P4VP RMs showed a positive potential with a stable structure (Figure S5b). At pH 2, the strong electrostatic interaction between hydrogen ions and pyridine groups led to interior structure tightening and a few coils in P4VP molecular chain, hence some dots and non-hollow structure could be observed in Figure S5a. As shown in Figure S5c, the P4VP-PEG-P4VP RMs were not stable in aqueous solution at pH 6. The zeta potential became negative in the pH region above 5.4. As reported previously, the pK_a value of P4VP at zero protonation is 5.0⁶. The potential became negative above pH 5.4, most likely due to the adsorption of anions OH^- , as suggested by several researchers⁷⁻⁹.

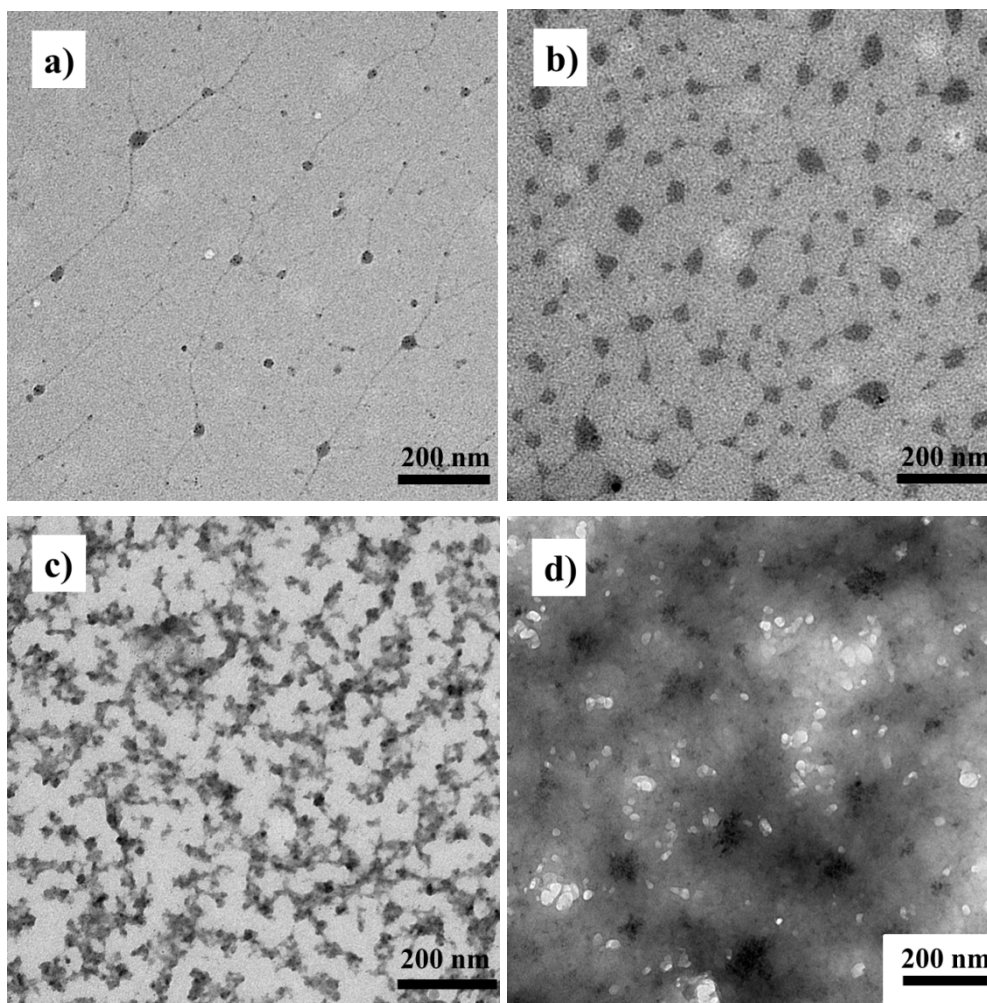


Figure S6. TEM images of a) shell cross-linked P4VP-PEG-P4VP reverse micelles by BIEE with the extent of cross-linking of a) 5%, b) 10%, c) 20% and d) 30%. The initial concentrations of the block copolymer P4VP-PEG-P4VP in mixed solution (mass ratio of 1-hexanol/water = 1) are 0.2mmol/L (equivalently polymer weight: 0.15 %).

The morphologies of SCRMs with different cross-linking densities were shown in Figure S6 (a-d). After crosslinking internally, the binding between P4VP-PEG-P4VP micelles was strengthened by the increasing content of cross-linking at the peripheral shell.

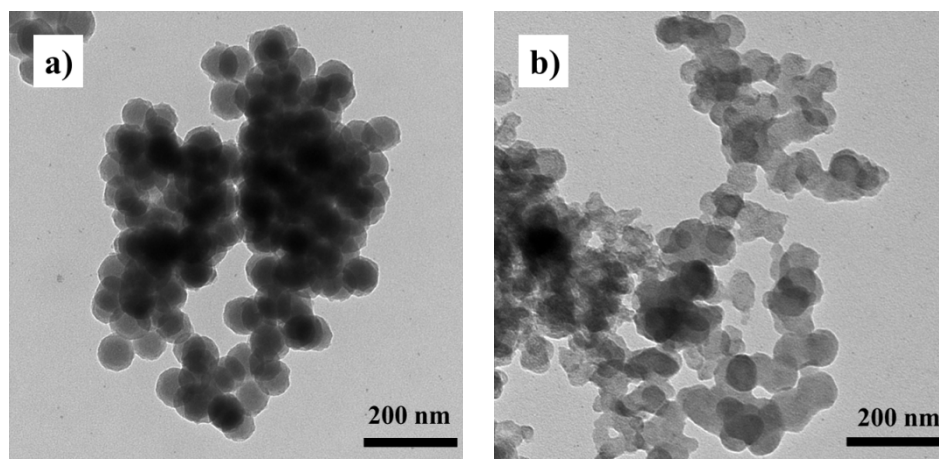


Figure S7. TEM images of a) self-assembled P4VP-PEG-P4VP micelles and b) shell cross-linked P4VP-PEG-P4VP micelles by BIEE with the extent of cross-linking of 30%. The initial concentrations of the triblock copolymer P4VP-PEG-P4VP in 1-hexanol/water mixture solution (1-hexanol/water = 1) are 0.5mmol/L.

To clearly investigate the morphology of shell-cross-linked, we increased the initial concentration (0.2mmol/L) to 0.5mmol/L. In Figure S4a, it could be found that P4VP-PEG-P4VP micelles tended to aggregate at this concentration. And after crosslinking, a larger SCRM aggregation with stronger binding could be investigated in Figure S4b, indicating that the cross-linking of the exterior layer proceeded through not only intramicrosphere reaction but also intermicrosphere reaction.

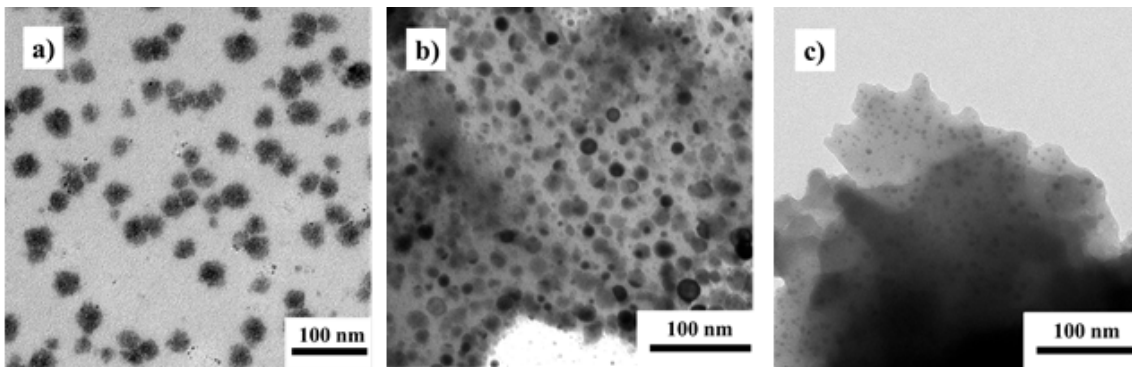


Figure S8. TEM images of CuCl_2 -(P4VP-PEG-P4VP) SCRMs (Cu: P4VP = 1:1) in 1-hexanol at the initial concentration of 0.5 mmol/L: a) fresh catalyst; b) after third reaction; c) after fifth reaction.

As shown in Figure S8, the reuse of the catalyst led to the broadening of film connecting to SCRMs. These might reduce the functional sites and the stability of SCRMs, resulting in a lower catalytic activity.

References

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