Supporting Information

Facile Intramolecular Crosslinking of Polymers by Metallic Coordination in Concentrated Solutions

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1. Experiment

1.1 Materials

N,N-dimethylformamide (DMF) was purchased from J&K Chemical. Hydrochloric acid (HCl, 37 vol%), aqueous ammonia ($NH_3 \cdot H_2O$, 28 wt%), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2$) were purchased from Sinopharm Chemical Reagent. 1,5-diiodopentane (DIP), ethylene diamine tetraacetic acid (EDTA) were purchased from TCI. Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) and $P4VP_{60k}$ were purchased from Sigma-Aldrich. PS_{93k}-*b*-$P4VP_{35k}$ and PS_{60k}-*b*-$P4VP_{32k}$-*b*-$PEO_{39.5k}$ were purchased from Polymer Source. Dialysis bag (Molecular weight cutoff=3500 D) was purchased from Viskase. All the reagents were used as received.

1.2 Intramolecular crosslinking the P4VP contained polymers with metallic ions.

In a typical experiment, $P4VP_{60k}$ (100 mg, 1.67×10^{-3} mmol) was dissolved in DMF (6.0 mL). 380 μL aqueous HCl (1M, 0.38 mmol) was diluted to 2.0 mL DMF and dropped into the solution for protonation of P4VP at 25 °C within 2 min. 23 mg of copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (0.095 mmol) was dissolved in 2.0 mL of DMF was dropped under stirring at 800 rpm within 3 min at 25 °C for the crosslinking. The crosslinking was performed at a concentration of 10 mg/mL. The crosslinked single chain nanoparticle (SCNP) of *c*P4VP was achieved by freeze drying the dispersion after

dialysis against water for 48 h.

1.3 Covalent crosslinking the *c*P4VP with DIP.

In a typical experiment, the Cu^{2+} crosslinked *c*P4VP$_{60k}$ (20 mg) was dispersed in DMF at a concentration of 10 mg/mL. After a given amount of DIP (2.3 μL, 0.015 mmol) was fed, the dispersion was stirred at 60 °C for 4 h. The DIP crosslinked SCNP was achieved by freeze drying after the dialysis.

1.4 Decomplexation of the *c*P4VP with EDTA.

In a typical experiment, the Cu^{2+} crosslinked *c*P4VP$_{60k}$ (20 mg) was dispersed in DMF at a concentration of 10 mg/mL. EDTA solution in water (pH=8) (10 mL, 40 mg/mL) was fed and stirred for 2 h. After dialysis, the precipitation in the dialysis bag was washed by aqueous NaOH and water for 3 times. The *c*P4VP nanoparticles were recovered into polymer chains after freeze-drying.

1.5 Synthesis of the composite SCNP of *c*P4VP@Fe_3O_4.

P4VP$_{60k}$ (20 mg) was dissolved in DMF (2.0 mL) and degassed with nitrogen for 1 h. After the protonation with aqueous HCl in DMF at a molar ratio of 0.4:1.0, the mixture of $FeSO_4 \cdot 7H_2O$ (3.0 mg) and $FeCl_3 \cdot 6H_2O$ (5.2 mg) (molar ratio 1.0:1.8) was fed for the intramolecular crosslinking. After the dispersion was heated to 80 °C, a desired amount of aqueous ammonia was fed to adjust pH~10. After stirring for 1 h, the composite SCNP of *c*P4VP@Fe_3O_4 was achieved after collection with a magnet.

1.6 Characterization.

Size and zeta potential were measured in DMF by dynamic light scattering at 25 ℃ on Malvern Zeta sizer Nano ZS90 with the measurement range of 0.3 nm-5 μm. All the samples were diluted to 1 mg/mL and measured without filtration. TEM characterization was performed on JEOL 1011 operating at 100 kV. The sample was diluted to 1 mg/mL with DMF and dropped onto the ultra-thin carbon film. Size statistical analysis of the TEM images was conducted by the Image J among 180 SCNP samples.

2. Results and Discussion

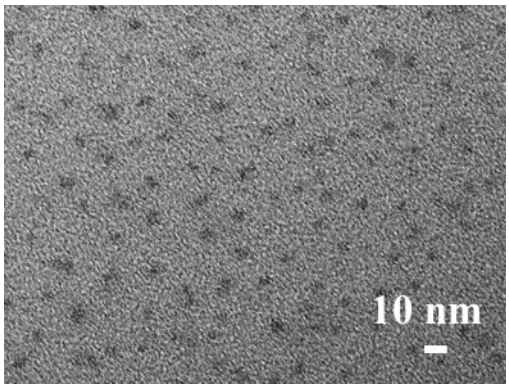


Figure S1. TEM image of the *c*P4VP$_{60k}$ after the intramolecular crosslinking with Cu^{2+} in an extremely dilute solution at 0.01 mg/mL.

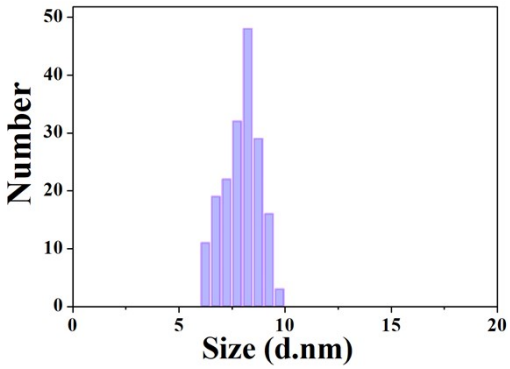


Figure S2. Image J statistical diameter of cP4VP$_{60k}$ coordinated with Cu^{2+}.

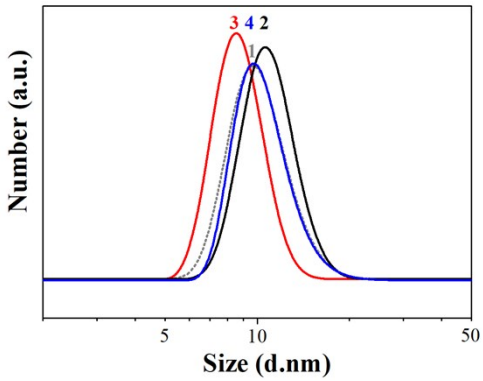


Figure S3. DLS traces of (1) P4VP$_{60k}$ in DMF, (2) the protonated P4VP$_{60k}$ at a degree of 40%, (3) *c*P4VP$_{60k}$ after crosslinking with Cu^{2+} and (4) the protonated P4VP$_{60k}$ in the presence of LiBr in DMF solution (the concentration of LiBr in DMF was 50 mmol/L).

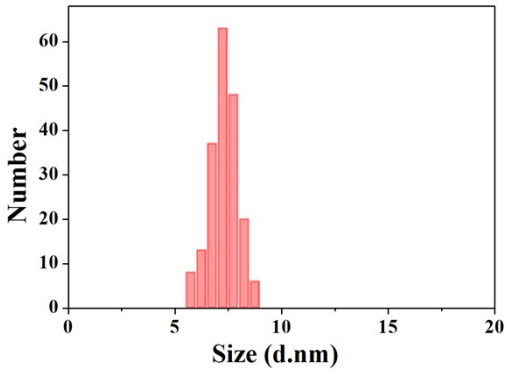


Figure S4. Image J statistical diameter of the cP4VP$_{60k}$ coordinated with Fe^{3+}.

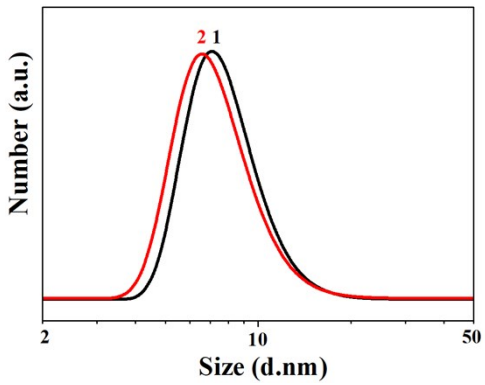


Figure S5. DLS traces of (1) the cP4VP$_{60k}$ after the electrostatic-mediated intramolecular crosslinking with Fe^{2+}/Fe^{3+}at the polymer concentration of 10 mg/mL and (2) the derived *c*P4VP@Fe_3O_4 composite nanoparticle.

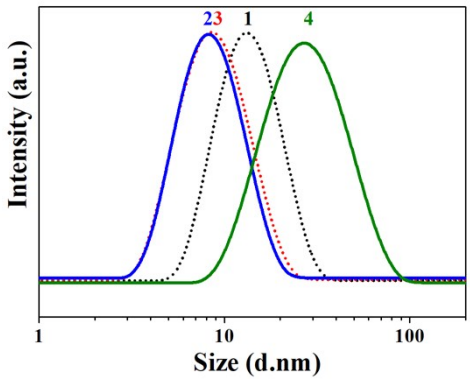


Figure S6. Intensity versus size DLS traces of (1) P4VP$_{60k}$, (2) the reference SCNP formed in the dilute solution, after electrostatic-mediated intramolecular crosslinking the P4VP$_{60k}$ with Cu^{2+} at varied contents: (3) 3% and (4) 4%.

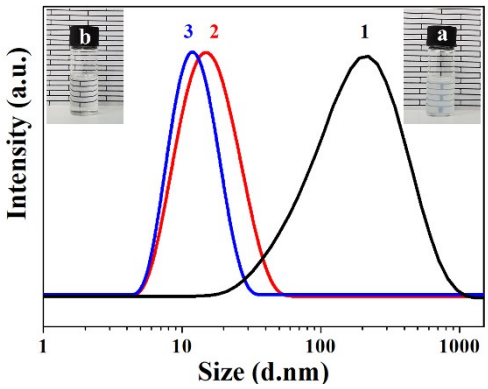


Figure S7. (1) DLS trace of the turbid system (a) at a higher (70%) protonation of $P4VP_{60k}$ in DMF; (2) the transparent solution (b) after feeding LiBr to the turbid system and (3) after the intramolecular crosslinking with Cu^{2+}.

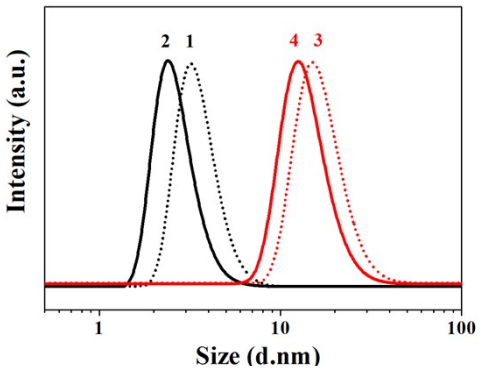


Figure S8. DLS traces of (1) $P4VP_{6k}$ and (2) after the intramolecular crosslinking with 10% of Cu^{2+}; (3) $P4VP_{170k}$ and (4) after the intramolecular crosslinking with 10% of Cu^{2+}. The molar content of H^+ was fixed at 40%.

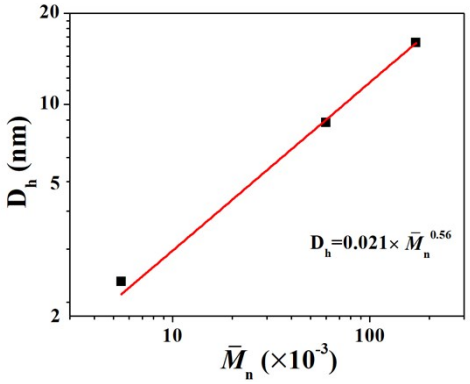


Figure S9. Hydrodynamic diameter (D_h) dependence of the derived *c*P4VP on number average molecular weight (M_n) of P4VP.

Figure S10. (a) Cu^{2+}crosslinked *c*P4VP$_{60k}$ dispersion in DMF and (b) after feeding EDTA and dialysis.

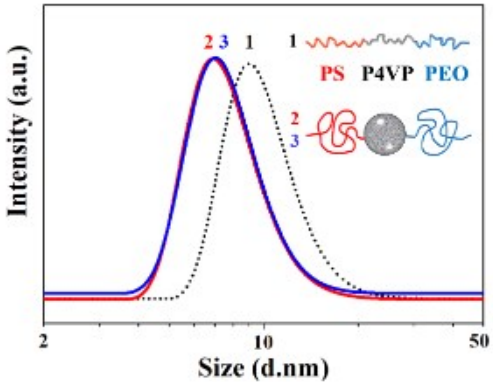
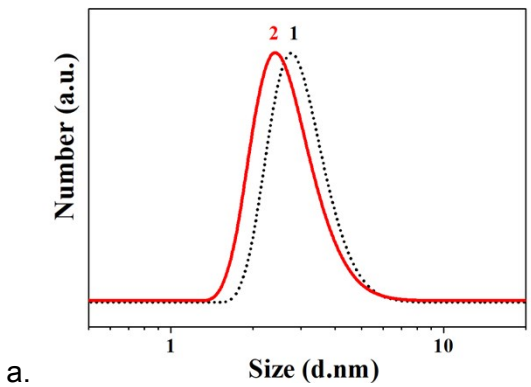
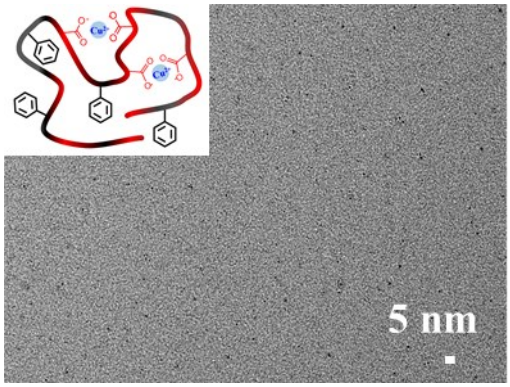


Figure S11. DLS traces of (1) PS$_{60k}$-*b*-P4VP$_{32k}$-*b*-PEO$_{39.5k}$ in DMF and the two SCNPs by the electrostatic-mediated crosslinking at polymer concentrations (mg/mL): (2) 50, (3) 80.



a.



b.

Figure S12. (a) DLS traces of (1) the SMA in DMF and (2) the *c*SMA SCNP after the electrostatic-mediated intramolecular crosslinking with Cu^{2+} at the polymer concentration of 10 mg/mL; (b) TEM image of the *c*SMA SCNP and the inset scheme.