Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Multi-stimuli Responsive Bottlebrush-Colloid Janus Nanoparticles Toward Emulsion Interfacial Manipulation and Catalysis

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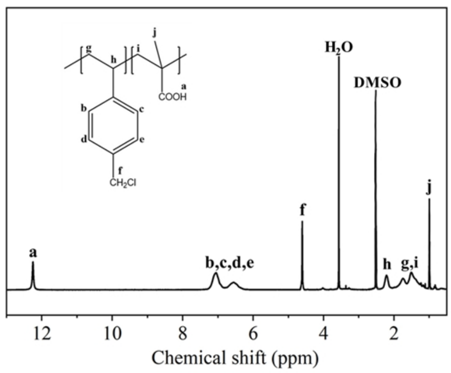


Fig. S1 ^{1}H NMR spectrum of $PVBC_{11.0k}$-*b*-$PMAA_{11.2k}$.

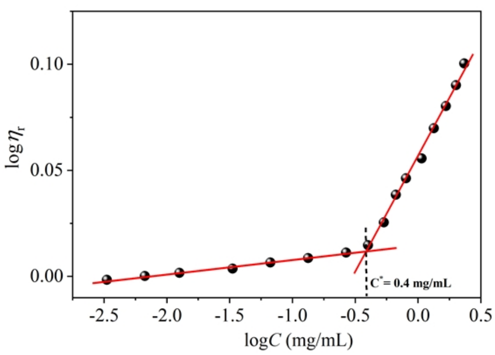


Fig. S2 Relationship between relative viscosity and the concentration of $PVBC_{11.0k}$-*b*-

PMAA$_{11.2k}$ solution in DMF, deviating from the Einstein's viscosity equation at 0.4 mg/mL.

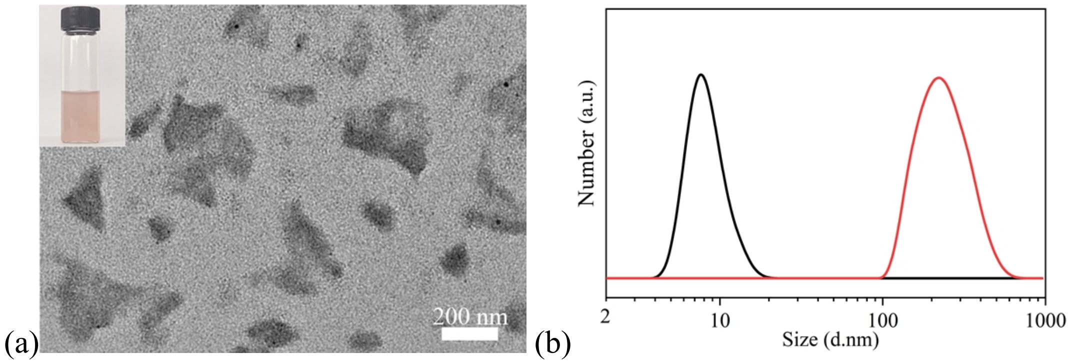


Fig. S3 (a) TEM image and (b) DLS trace of PVBC-*b*-PMAA after crosslinking with Co^{2+} at a polymer concentration of 10 mg/mL.

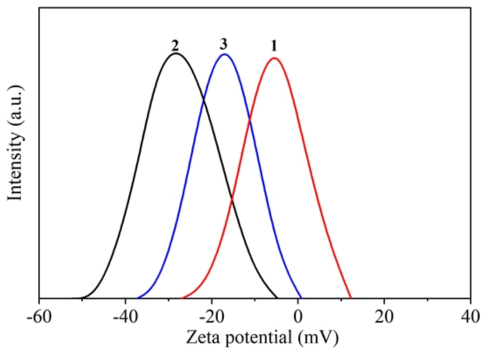


Fig. S4 Zeta potential of (1) PVBC-*b*-PMAA in DMF, (2) after the deprotonation by adding NaOH and (3) after the crosslinking with Co^{2+}.

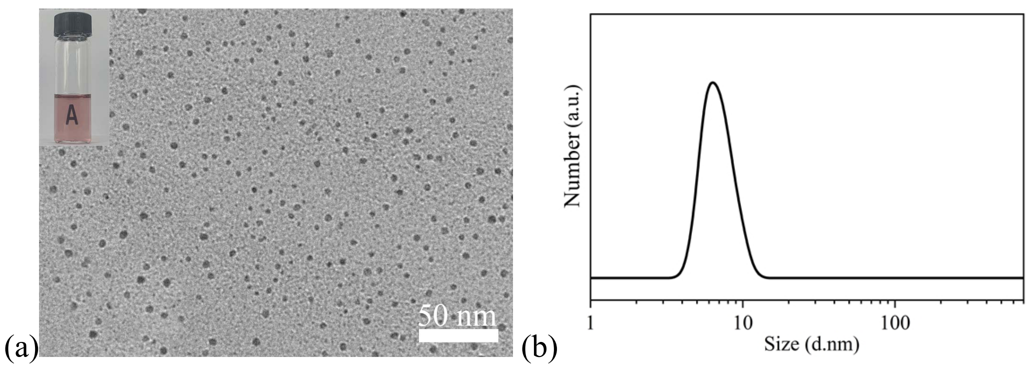


Fig. S5 (a) TEM image and (b) DLS trace of PVBC-*b*-PMAA after electrostatic-mediated intramolecular crosslinking with Co^{2+} at a polymer concentration of 10 mg/mL.

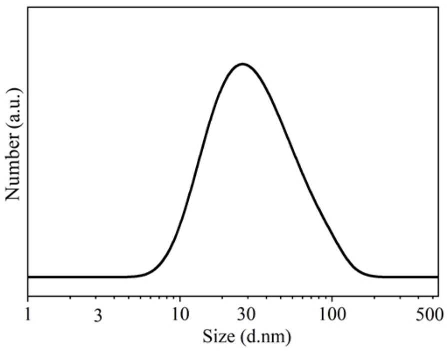


Fig. S6 DLS trace of PVBC-*b*-PMAA after electrostatic-mediated intramolecular crosslinking with Co^{2+} (22% molar ratio with respect to MAA) at a polymer concentration of 30 mg/mL.

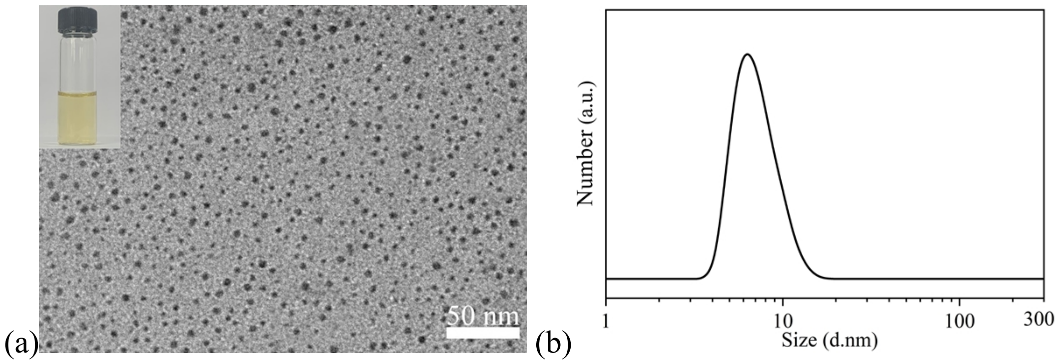


Fig. S7 TEM image (a) and DLS trace (b) of PVBC-*b*-PMAA after electrostatic-mediated intramolecular crosslinking with K_2PdCl_4 at a polymer concentration of 30 mg/mL.

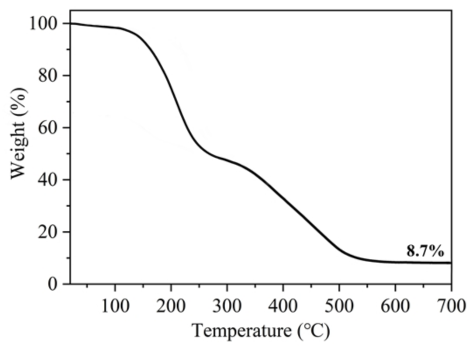


Fig. S8 TGA trace of PVBC-cPMAA@Co.

For PVBC-cPMAA@Co, the theoretic weight fraction of cobalt can be calculated as:

$f_{Co}=m_{Co}/(m_{Co}+m_{polymer})\times100\%$

In the experimental section, 21.0 mg (0.071 mmol) of $Co(NO_3)_2\cdot6H_2O$ was reacted with 60 mg (2.73×10^{-3} mmol) of $PVBC_{11k}$-*b*-$PMAA_{11.2k}$. The weight fraction of Co in $Co(NO_3)_2\cdot6H_2O$ is 0.203. Therefore, the theoretical of $m_{Co}=21\times0.203=4.26$ mg in the final product. The theoretical weight of PVBC-cPMAA@Co=m_{Co}+$m_{polymer}$=4.26+60=64.26 mg. The theoretical cobalt weight ratio is: f_{Co} = 4.26/64.26×100% =6.6%.

The TGA is conducted in air to achieve a full elimination of the polymer, and the final product is Co_3O_4.[1] Therefore, the weight fraction of Co in the PVBC-cPMAA@Co is 177/241×8.7%=6.4%, which is in a good agreement of the theoretical value.

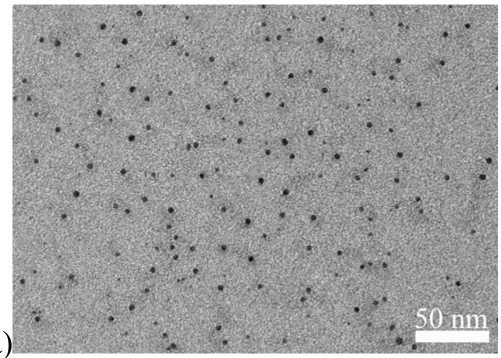
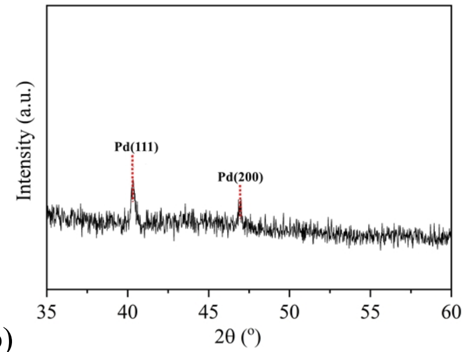
(a)  (b) 

Fig. S9 TEM image (a) and XRD pattern (b) of PVBC-cPMAA@Pd after reduction.

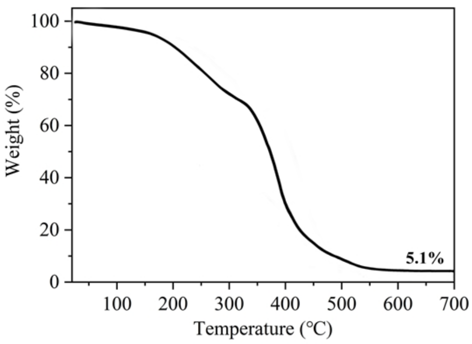


Fig. S10 TGA trace of PVBC-cPMAA@Co-PDMEAMA.

Calculation of the weight faction of PDMEAMA:

The weight fraction of Co in the PVBC-cPMAA@Co-PDMEAMA JNP is 177/241×5.1%=3.7%. The weight ratio of the total polymer to Co is 96.3/3.7=26.027. The weight ratio of the PVBC-cPMAA to Co is 93.6/6.4=14.625 based on the TGA data in Fig. S8. The weight ratio of PDMEAMA to Co is 26.027-14.625=11.402. Therefore, the weight fraction of PDMEAMA in PVBC-cPMAA@Co-PDMEAMA is 11.402/(26.027+1)×100% =42.1%.

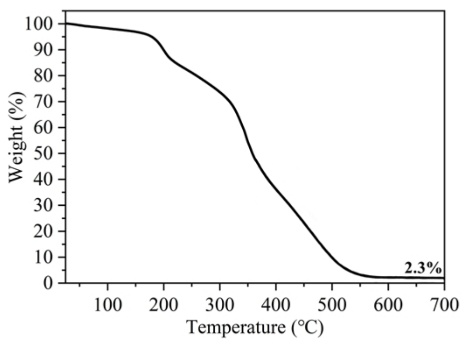


Fig. S11 TGA trace of PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA.

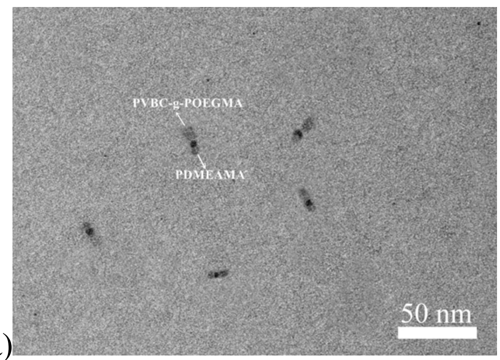
Calculation of the weight faction of PNIPAM:

The weight fraction of Co in the PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA JNP is 177/241×2.3%=1.7%. The weight ratio of total polymer to Co is 98.3/1.7=57.824. The weight ratio of the polymer of PVBC-cPMAA and PDMEAMA to Co is 26.027 as calculated in Fig. S10. The weight ratio of the PNIPAM to Co is 57.824-26.027=31.796. Therefore, the weight fraction of PNIPAM in PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA is 31.796/(57.824+1)×100%=54.1%. The weight fraction of PDMEAMA in PVBC-cPMAA@Co-PDMEAMA is 42.1% as calculated in Fig. S12. Therefore, the weight fraction of PDMEAMA in PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA is (1-0.541)*0.421*100%=19.3%. The weight ratio of PNIPAM/PDMEAMA=51.4/20.4=2.8/1.0.

Calculation of the average DP of the grafted PNIPAM side chain:

The weight fraction of PVBC to Co is 11000/(11000+112000)×93.6/6.4=7.247 based on the TGA data in Fig. S6. The number of repeat unit of VBC is 11000/M_{VBC}(152.5)=72. The weight ratio of PNIPAM/PVBC=31.796/7.247=4.371/1=72×M_{NIMA}(113)×$\mathrm{DP}_{\mathrm{PNIPAM}}$/11000

$\mathrm{DP}_{\mathrm{PNIPAM}}$ is calculated to be ~6.

(a)


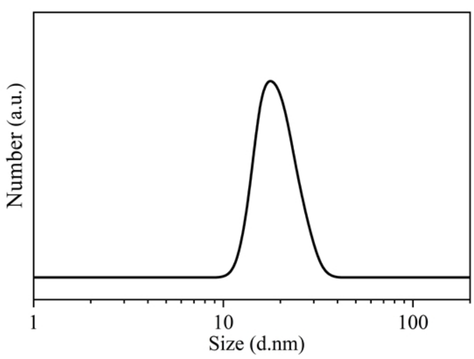
(b)


Fig. S12 TEM image (a) and DLS trace (b) of PVBC-*g*-POEGMA-cPMAA@Co-PDMEAMA.

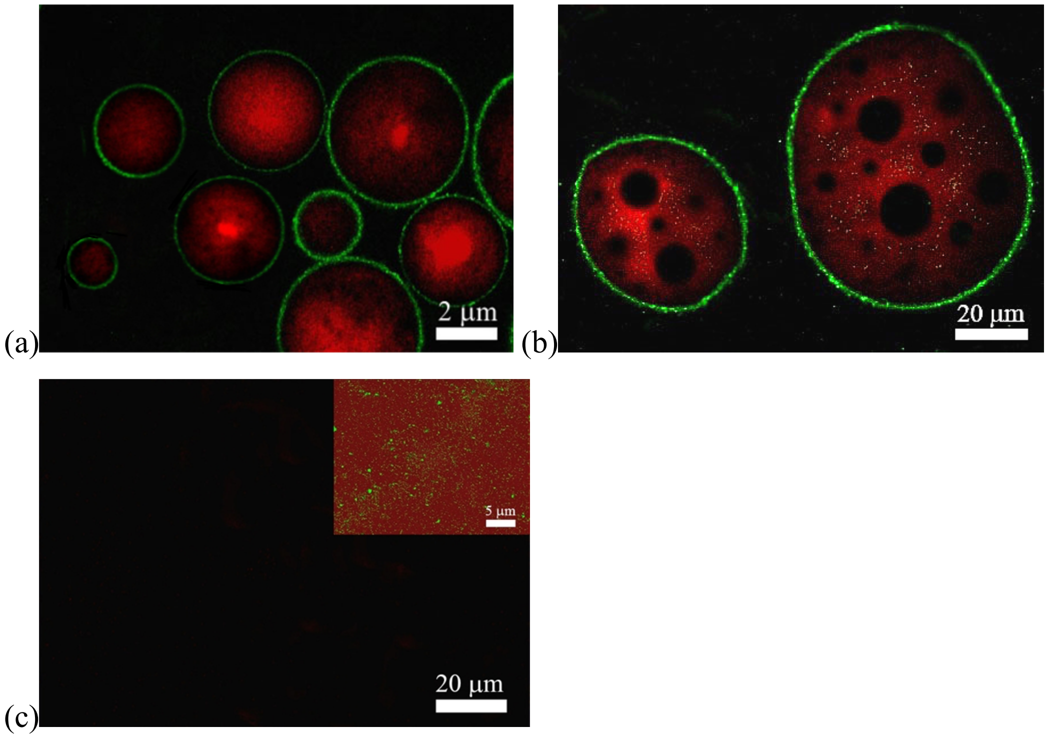


Fig. S13 (a) Toluene/water emulsion stabilized with the PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA JNP at 35 °C, pH=6 and (b) after increasing pH to 8; (c) CLSM images of bottom aqueous phase and inset the top oil phase after de-emulsification.

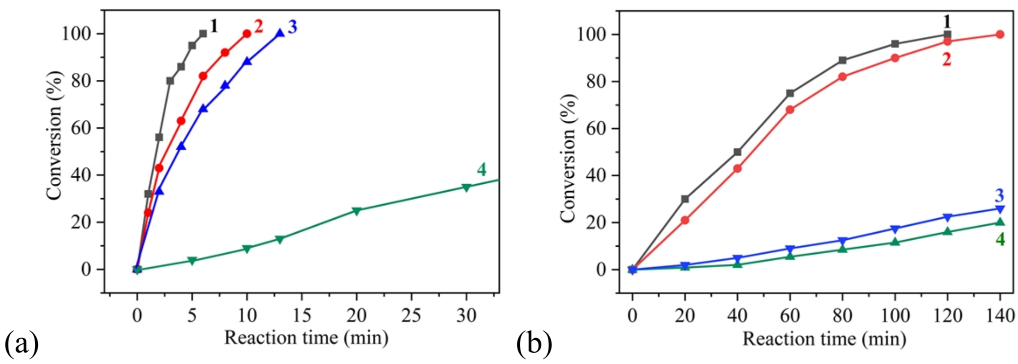


Fig. S14 (a) The conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in aqueous solution along increasing reaction time, catalyzed by PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA JNP at (1) 25 °C, pH=6, (2) 35 °C, pH=6, (3) 25 °C, pH=8 and (4) 35 °C, pH=8; (b) The conversion of nitrobenzene to aniline along increasing reaction time, catalyzed by PVBC-*g*-PNIPAM-cPMAA@Co-PDMEAMA JNP at (1) 35 °C, pH=6, (2) 25 °C, pH=8, (3) 25 ^{o}C, pH=6 and (4) 35 ^{o}C, pH=8.

References

1. T. Zhou, T. Zhang, J. Deng, R. Zhang, Z. Lou and L. Wang, *Sensor Actu. B-Chem.*, 2017, **242**, 369-377.