

Supporting information

Large Scale Synthesis of Single-Chain/Colloid Janus Nanoparticles with Tunable Composition

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1. Experiment

1.1 Materials. PS_{5.2k}-*b*-PAA_{4k} (PDI=1.15) was purchased from Polymer Source. DMF, 1-methylimidazole (MI), 1,6-hexanedithiocyanate (HDI), 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50), N-isopropylacrylamide (NIPAM), N,N-dimethylacetamide (DMA), dimethyl sulfoxide-d₆ (DMSO-d₆), 2-diethylaminoethyl methacrylate (DEAEMA), 9-(diethylamino)benzo[a]phenoxazin-5(5H)-one (Nile Red) were purchased from J&K. N,N'-Dicyclohexylcarbodiimide (DCC) and N-hydroxysuccinimide (NHS) were purchased from Alfa Aesar. Sodium hydroxide (NaOH), aqueous ammonia (NH₃·H₂O, 28 wt%), ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous sulfate heptahydrate (FeSO₄·7H₂O) and nickel nitrate (Ni(NO₃)₂·6H₂O) were purchased from Sinopharm Chemical Reagent. Sodium borohydride

(NaBH₄) was purchased from Beijing Chemical Works. All the other reagents were used as received.

1.2 Synthesis of the PS-*c*PAA JNP. PS_{5.2k}-*b*-PAA_{4k} was dissolved in anhydrous DMF at varied concentration. After MI was added into the solution at a MI/PAA molar ratio of 0.5/1.0, the complexation between MI and PAA was performed under stirring at 25 °C for 24 h. After HDI was dropped into the solution at the HDI/AA molar ratio of 0.2/1.0, the crosslinking was performed under stirring at 25 °C for 24 h. After the crosslinking, MI was removed from the complex by dialysis against water at 55 °C for 24 h. After freeze-drying, the JNP of PS-*c*PAA was achieved.

1.3 Synthesis of the PS-*c*PAA@AIBA JNP. After the saturated aqueous solution of V-50 was treated with sodium hydroxide for alkalization, AIBA was derived by crystallization at 5 °C and freeze-drying. After the PS-*c*PAA JNP (10.0 mg) was dispersed in anhydrous DMF (5.0 mL), DCC/NHS (molar ratio of 1.0/0.5) was added under stirring at 25 °C for 12 h to activate the carboxyl group. AIBA solution in anhydrous DMF (AIBA/DCC molar ratio of 0.5/1.0) was added under stirring for the amidation for 12 h. DCC and NHS were removed by dialysis against DMF. The composite JNP of PS-*c*PAA@AIBA was achieved after freeze-drying.

1.4 Synthesis of the PS-*c*PAA@(Fe₃O₄-PNIPAM) composite JNP. PS-*c*PAA@AIBA JNP (5.0 mg) was dissolved in anhydrous DMF (5.0 mL). After FeCl₃·6H₂O solution in DMF (370.0 μL, 50.0 mg/mL) and FeSO₄·7H₂O solution in DMF (370.0 μL, 50.0 mg/mL) were added, the mixture was stirred at room temperature for 2 h in Ar. After loading the ions inside the *c*PAA domain, 2.0 mL of NH₃·H₂O was added for the reaction at 50 °C for 30 min to form Fe₃O₄. NIPAM (102.0 mg) was added for the polymerization at 80 °C for 8 h, while crystallinity of the Fe₃O₄ was improved.

N,N-dimethylacetamide (DMA, 84.0 mg) was fed during the polymerization as an internal standard to estimate the polymerization degree. The JNP of PS-*c*PAA@(Fe_3O_4 -PNIPAM) composite was collected with a magnet after centrifugation at 1000 rpm for 1 min.

1.5 Performance of the PS-*c*PAA@(Fe_3O_4 -PNIPAM) composite JNP. 100.0 μL of toluene and 1.0 mL of water were ultrasonicated forming an oil/water emulsion in the presence of the PS-*c*PAA@(Fe_3O_4 -PNIPAM) JNP (10.0 mg). Stability and magnetic manipulation of the emulsion were systematically characterized. A trace amount of Nile Red (9-(diethylamino)benzo[*a*]phenoxazin-5(5H)-one) was fed to dye toluene for easier observation.

1.6 Characterization. Size and zeta potential were measured by dynamic light scattering (DLS: Malvern Zetasizer Nano ZSE). Morphology of the samples was characterized by transmission electron microscopy (TEM: JEOL 1011 operating at 100 kV). Phosphotungstic acid (PTA) aqueous solution (10.0 μL , 2.0 wt%) was used to selectively stain the PAA block. Fourier transform infrared (FT-IR) spectra were recorded on the sample-/KBr-pressed pellets using a Bruker Equinox 55 instrument at room temperature. Bruker 400III spectrometer was used to record the ^1H NMR spectra. The magnetic property was measured using vibrating sample magnetometer (VSM: PPMS-9). The crystallinity was characterized by X-ray powder diffraction (XRD) on Rigaku D/max-2500. Morphology of the emulsion droplets was observed under OLYMPUS FV1000-IX81 microscope at a laser wavelength of 561.8 nm. Transmittance (at a wavelength of 500 nm) of the JNP aqueous dispersion (0.5 mg/mL) was measured on UV-2550 UV-vis spectrophotometer to characterize the thermal responsive behavior. The dispersion was scanned from 28 $^\circ\text{C}$ to 45 $^\circ\text{C}$ at a rate of 0.2 $^\circ\text{C}/\text{min}$. The JNP contained water droplet pendent in toluene technique was used to measure interfacial tension on KRÜSS DSA30. During the

irradiation of the dispersion (1.0 mg/mL) under 808 nm laser (0.6 W/cm²), temperature was monitored with infrared camera (FLIR i7) imaging.

2. Results and Discussion

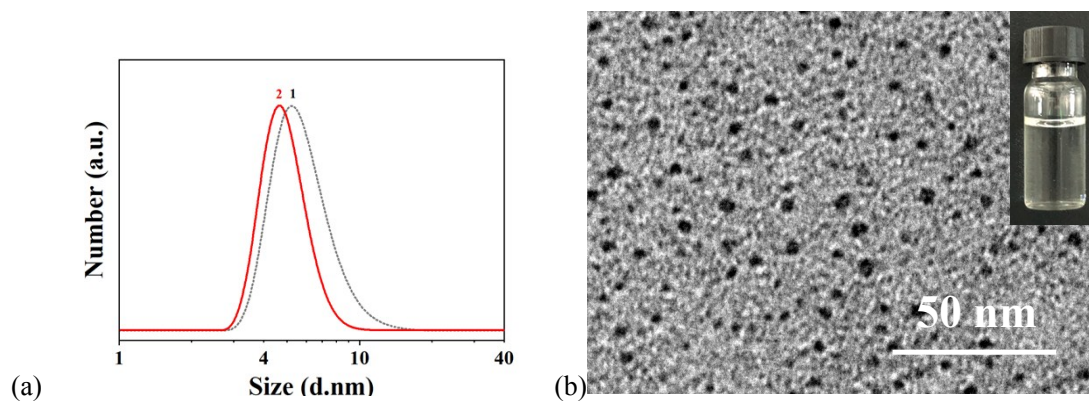


Fig. S1 (a) DLS traces of (1) PS_{5.2k}-*b*-PAA_{4k} and (2) the PS-*c*PAA JNP by the intramolecular crosslinking at 0.1 mg/mL. (b) TEM image of the PS-*c*PAA JNP after staining with PTA.

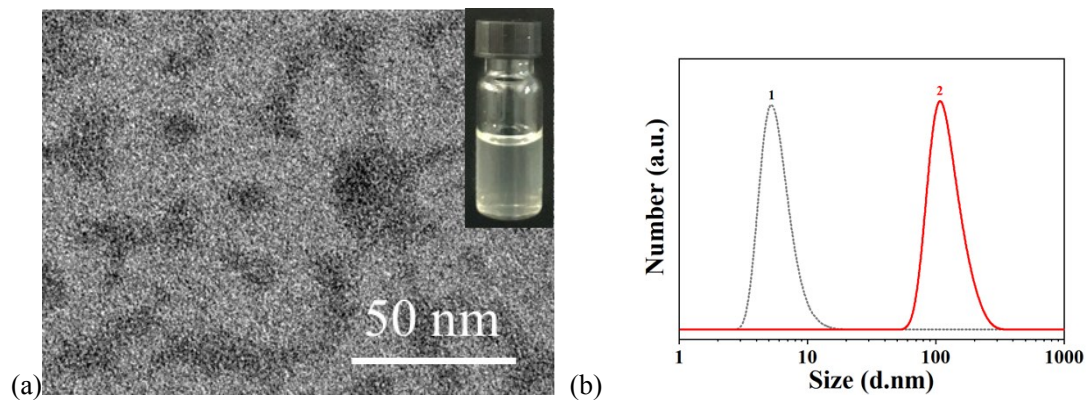


Fig. S2. (a) TEM image of the sample after crosslinking at 5 mg/mL. (b) DLS traces of (1) PS_{5.2k}-*b*-PAA_{4k} and (2) the sample after crosslinking at 5 mg/mL.

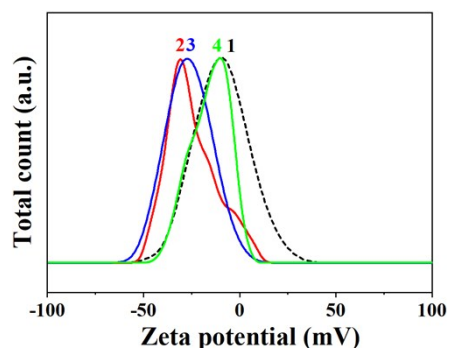


Fig. S3. Zeta potential traces of: (1) PS_{5.2k}-*b*-PAA_{4k}, (2) after modifying with MI, (3) PS-*c*PAA JNP by electrostatic-mediated crosslinking and (4) after removal of MI.

The PS_{5.2k}-*b*-PAA_{4k} is nearly neutral with a zeta potential around -8.0 mV (trace 1), which becomes highly negative with a Zeta potential of -30.0 mV after the modification with MI (trace 2). The PS-*c*PAA JNP by the intramolecular crosslinking remains highly negative (trace 3). After the removal of MI, the highly negative PS-*c*PAA JNP becomes nearly neutral with a zeta potential of -8.0 mV (trace 4).

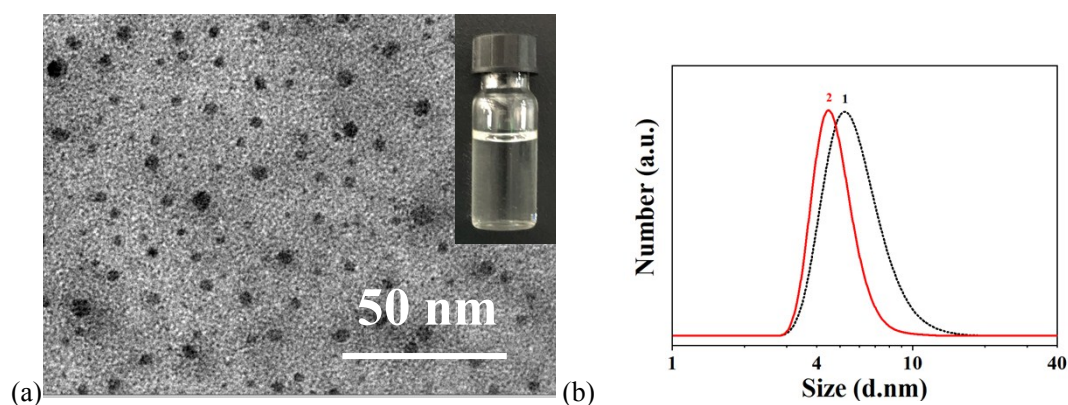


Fig. S4. (a) TEM image of the PS-*c*PAA JNP by the electrostatic-mediated intramolecular crosslinking at 5.0 mg/mL. (b) DLS traces of (1) PS_{5.2k}-*b*-PAA_{4k} and (2) the PS-*c*PAA JNP.

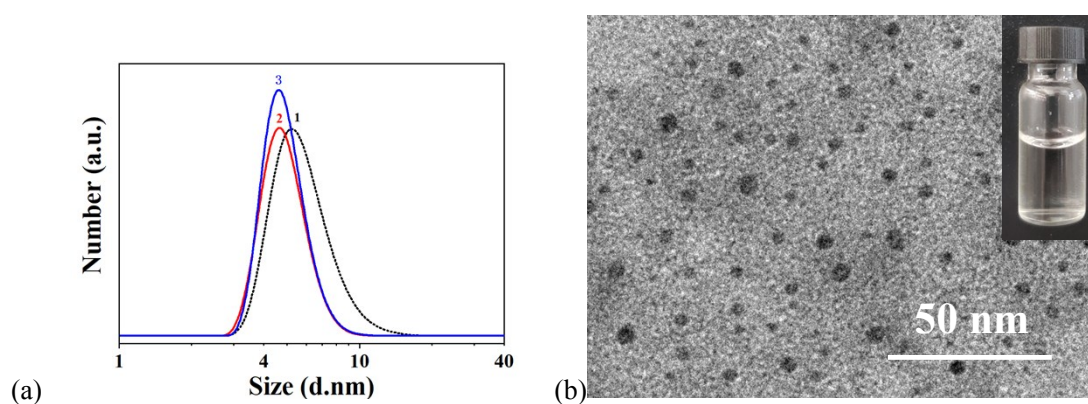


Fig. S5 (a) DLS traces of (1) PS_{5.2k}-*b*-PAA_{4k} and (2) the PS-*c*PAA JNP by the intramolecular crosslinking at 0.1 mg/mL, and (3) the PS-*c*PAA JNP by the electrostatic-mediated intramolecular crosslinking at 50 mg/mL. (b) TEM image of the PS-*c*PAA JNP by the electrostatic-mediated intramolecular crosslinking at 50 mg/mL.

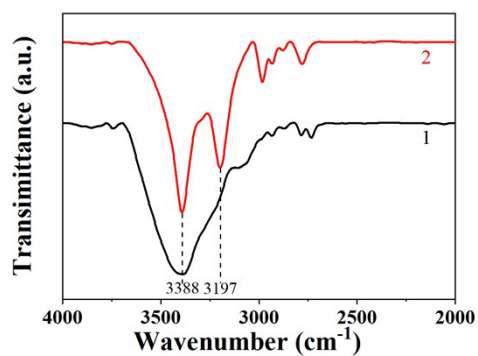


Fig. S6. FT-IR spectra of: (1) V-50 and (2) AIBA. The broad peak at 3000~3600 cm^{-1} assigned to ammonium salt of V-50 disappears after the alkalization to derive AIBA, and the characteristic double peaks at 3197 cm^{-1} and 3388 cm^{-1} assigned to the amino group of AIBA appear.

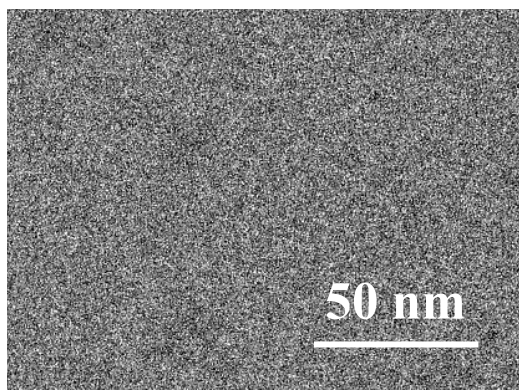


Fig. S7. TEM image of the as-synthesized PS-cPAA@AIBA JNP without staining with PTA.

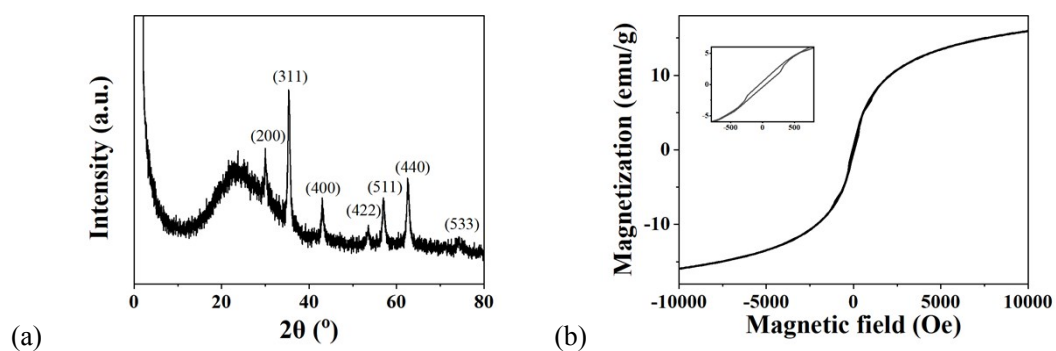


Fig. S8. (a) XRD pattern of the PS-cPAA@(Fe₃O₄-AIBA) composite JNP. (b) VSM trace of the PS-cPAA@(Fe₃O₄-AIBA) JNP.

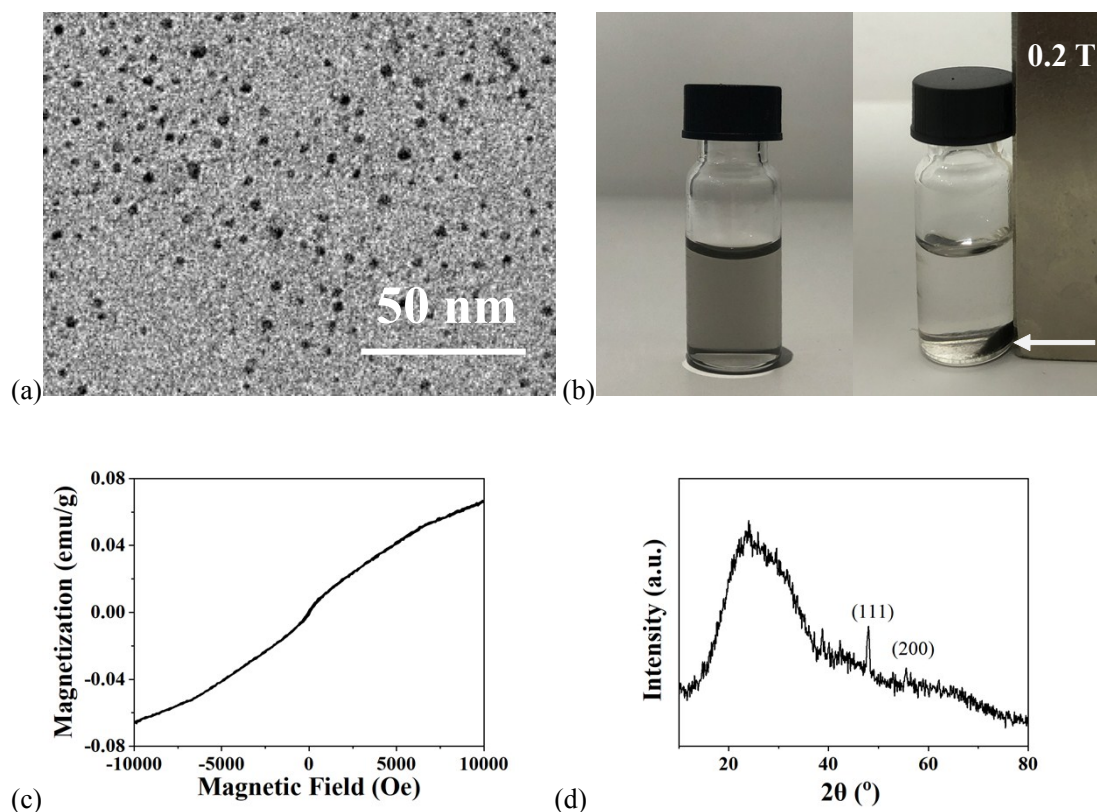
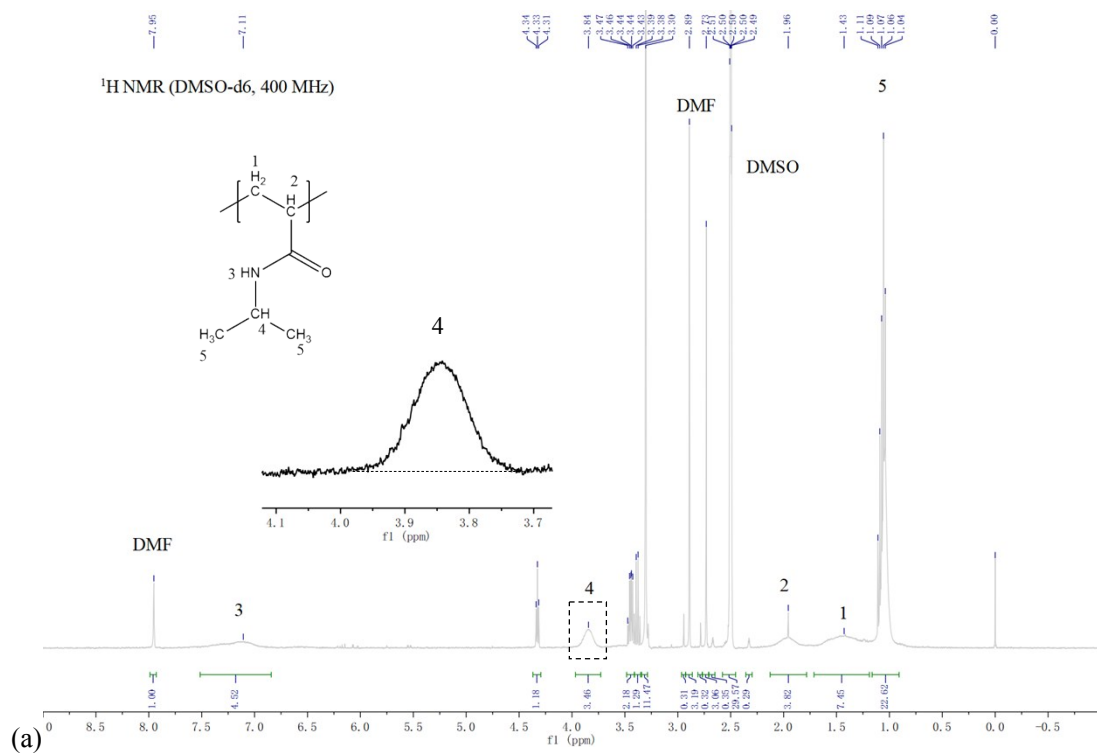
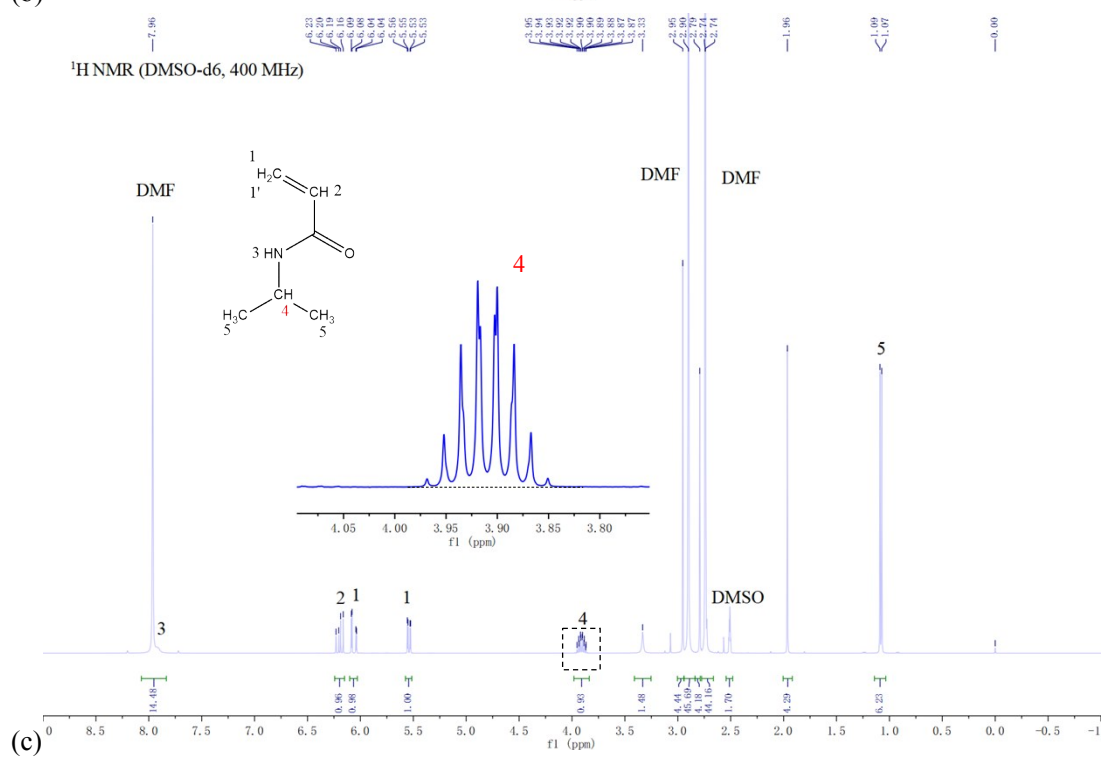
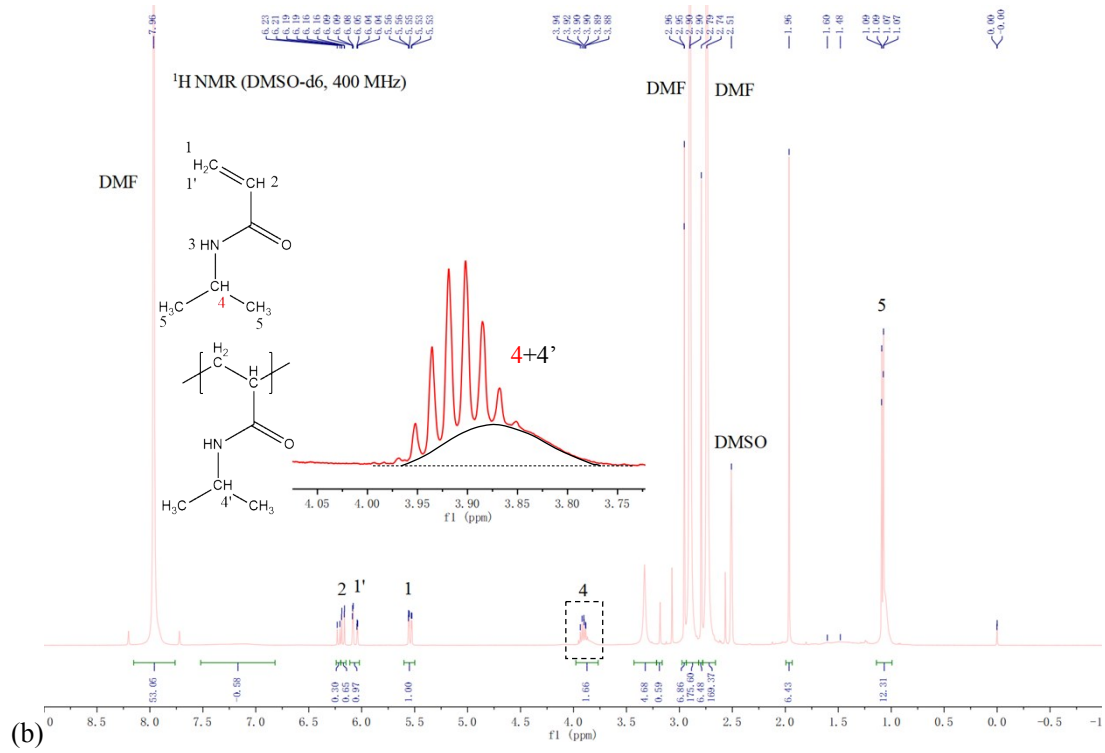


Fig. S9. (a) TEM image of the PS-cPAA@AIBA composite JNP after growing nickel. (b) PS-cPAA@(Ni-AIBA) composite JNP dispersion in DMF (left) and collection with a magnet (right). (c) VSM trace of the PS-cPAA@(Ni-AIBA) JNP. (d) XRD pattern of the PS-cPAA@(Ni-AIBA) JNP.





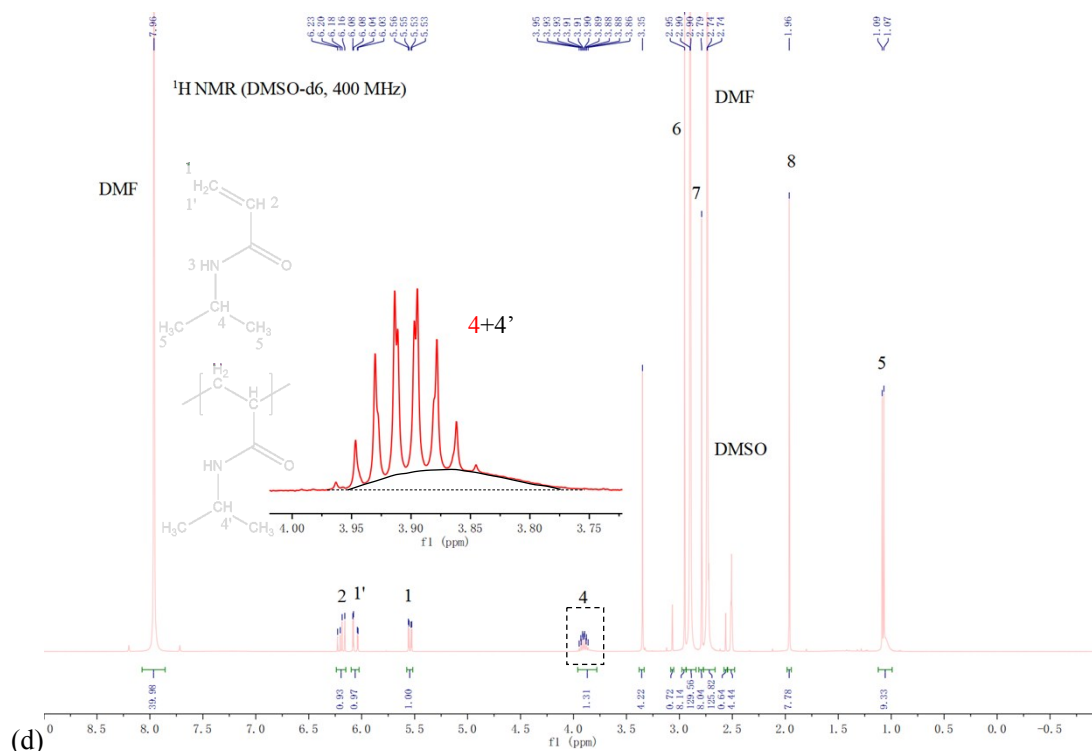


Fig. S10. ¹H-NMR spectra of: (a) PNIPAM, (b) the PS-*c*PAA@PNIPAM JNP dispersion against PS-*c*PAA@AIBA after the polymerization, the supernatants by isolating the PS-*c*PAA@(Fe₃O₄-PNIPAM) JNPs against the PS-*c*PAA@(Fe₃O₄-AIBA) at varied AIBA/AA molar ratio: (c) 0.2/1.0 and (d) 0.3/1.0.

DMA: the intense characteristic peak at $\delta=1.97$, as the internal standard to calculate the conversion.

NIPAM: the intense characteristic peaks at $\delta= 6.07, 5.55, 6.20$ ppm assigned to the vinyl protons (peak 1, 1', 2 in Fig. S8c), the intense characteristic peaks at $\delta=7.92$ ppm to the secondary amino group proton (peak 3 in Fig. S8c), the intense characteristic peak at $\delta=3.92$ ppm to the isopropyl proton (peak 4 in Fig. S8c), and the intense characteristic peak at $\delta=1.08$ ppm to the methyl protons (peak 5 in Fig. S8c).

PNIPAM: the broad characteristic peak at $\delta=1.20-1.70, 1.80-2.20$ ppm assigned to the backbone proton (peak 1, 2 in Fig. S8a), the broad characteristic peaks at $\delta= 7.00-7.50$ ppm to the secondary amino group proton (peak 3 in Fig. S8a), the broad characteristic peak at $\delta=3.75-4.00$ ppm assigned to the isopropyl proton (peak 4 in Fig. S8a), and the broad characteristic peak at $\delta=0.80-1.15$ ppm to the methyl protons (peak 5 in Fig. S8a).

When using the PS-*c*PAA@AIBA JNP achieved at the AIBA/AA molar ratio of 0.2/1.0, a composite JNP dispersion was derived after the polymerization. Both intense peaks assigned to residual monomer and broad peak assigned to PNIPAM are present in the dispersion (peak 4, 4' in Fig. S8b). The JNP and the residual monomer were separated by a complicated coprecipitation procedure.

When using the PS-*c*PAA@(Fe₃O₄-AIBA) JNP, the composite JNP was simply separated from the dispersion with a magnet and no broad peaks assigned to PNIPAM but residual monomer was observed (Fig. S8c). This implies that the polymerization is completely confined within the colloidal network with no free chains leaking outwardly. The monomer conversion was calculated

39.8 %.

When using another PS-*c*PAA@(Fe_3O_4 -AIBA) composite JNP achieved at a higher AIBA/AA molar ratio of 0.3/1.0, some amount of free PNIPAM is present in the supernatant (Fig. S8d). The free PNIPAM is originated from the polymerization out of the network by the dangled AIBA.

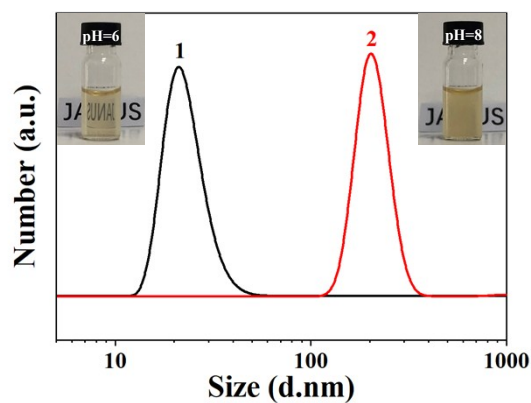


Fig. S11. DLS traces of the pH responsive PS-*c*PAA@(Fe_3O_4 -PDEAEMA) JNP in water at (1) pH=6 and (2) pH=8.