Synthesis of Ferromagnetic Polymer Coated Nanoparticles on Multi-gram Scale with Tunable Particle Size

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Supporting Information

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Experimental section

1. Materials and Characterization

Anhydrous 1,2-dichlrobenzene (DCB), toluene, *N*,*N*-dimethylformamide (DMF), methanol (MeOH), dichloromethane (DCM), 2-[4-(bromomethyl)phenyl]propanoic acid from Aldrich, neutral alumina, 2,2'-bipyridine (bipy), benzyl bromide from Alfa Aesar, and dicobaltoctacarbonyl ($Co_2(CO)_8$) from Strem Chemicals were purchased and used as received without further purification. Copper(I) bromide (98 %, Aldrich) was purified by stirring in glacial acetic acid overnight. Styrene (99 %, Aldrich) was passed through a short column of neutral alumina to remove inhibitors prior to use in polymerization reaction. Deoxygenation of styrene and *N*,*N*-dimethylformamide (DMF) was achieved by bubbling with argon gas for 30 minutes prior to use in polymerization reaction. Reaction temperatures were controlled using an IKAmag temperature modulator for polymerization reaction. Themolysis reactions were performed using an Omega CSC32 benchtop controller with K-type thermocouple and reported temperatures were measured in reaction mixtures. ^{1}H NMR spectra were obtained using a Bruker DRX 400 or 600 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are referenced to Me_4Si for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5-µm PLgel columns (Polymer Labs, pore size 10^4, 10^3 and 10^2 Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Enpower software (Waters), calibrated against low polydispersity linear polystyrene standards. Transmission electron microscopy (TEM) images were obtained on a JEM100CX II transmission electron microscope (JEOL) at an operating voltage of 60 kV or a Phillips CM12 transmission electron microscope at 80 kV, using in-house-prepared copper grid (Cu, hexagonal, 300 mesh). Analysis of images was carried out using ImageJ software (W. S. Rasban, National Institutes of Health, 1997-2007, http://rsb.info.nih.gov/ij/). Relative uncertainty of particle size determinations using ImageJ was found to be 1 % of the diameter average (*e.g.*, 20 ± 0.2 nm). Vibrating sample magnetometry (VSM) measurements were obtained using a waker HF 9H electromagnet with a Lakeshore 7300 controller and a Lakeshore 668 power supply. Magnetic measurements were carried out at room temperature (27 °C or 300 K) and low temperature (-223 °C or 50 K) with a maximum S-2 applied field of 1190 kA/m, a ramp rate of 2630 $Am^{-1}s^{-1}$ and a time constant of 0.1. X-ray diffraction (XRD) measurements were performed using the X'pert X-ray diffractometer (PW1827, Phillips) at room temperature with CuKα radiation source at 40 kV and 30 mA.

2. Syntheses of polymeric ligands and cobalt nanoparticles

2.1. Synthesis of Carboxylic acid End-Functionalized Polystyrene (PS-COOH)[1]

To an oven dried 125 mL Schlenk flask equipped with a stir bar were added Cu(I)Br (0.57 g, 4.0 mmol), 2-[4-(bromomethyl)phenyl]propanoic acid (0.97 g, 4.0 mmol) and bipy (1.3 g, 8.0 mmol). The flask was fitted with a rubber septum, evacuated and back-filled with argon for three cycles. Deoxygenated DMF (6 mL) was added *via* syringe and stirred until a red complex formed. Deoxygenated styrene (54 g, 60 mL, 520 mmol) was added *via* syringe to the reaction flask. The flask was placed in a thermostated oil bath held at 110 °C for 12 h to reach a monomer conversion of 80 %. The reaction mixture was diluted with dichloromethane (300 mL) and passed through a short alumina column to remove the copper catalyst. The polymer solution was washed with 10 % EDTA aqueous solution, dried over anhydrous $MgSO_4$, filtered and concentrated. The concentrated polymer solution was precipitated into stirring methanol three times, followed by drying *in vacuo* to yield a white powder (28 g, 65 % yield based on monomer conversion).

^1H NMR (600 MHz, $CDCl_3$) δ 7.20-6.30 (br, ArH), 2.25-1.20 (br, $CH+CH_2$), $M_{n\ SEC}$ = 12000 g/mol; M_w/M_n = 1.11.

2.2. Synthesis of Phenylethyl End-Functionalized Polystyrene

To an oven dried 25 mL Schlenk flask equipped with a stir bar were added Cu(I)Br (0.14 g, 1.0 mmol) and bipy (0.31 g, 2.0 mmol). The flask was fitted with a rubber septum, evacuated and back-filled with argon for three cycles. Deoxygenated styrene (13 g, 14 mL, 120 mmol) and benzyl bromide (0.17 g, 1.0 mmol) were added *via* syringe to the reaction flask. The flask was placed in a thermostated oil bath held at 110 °C for 14 h to reach a monomer conversion of 85 %. The reaction mixture was diluted with dichloromethane (50 mL) and passed through a short alumina column to remove the copper catalyst. The polymer solution was washed with 10 % EDTA aqueous solution, dried over anhydrous $MgSO_4$, filtered and concentrated. The concentrated polymer solution was precipitated into stirring methanol three times, followed by drying *in vacuo* to yield a white powder (7.6 g, 68 % yield based on monomer conversion).

^1H NMR (400 MHz, $CDCl_3$) δ 7.25-6.25 (br, ArH), 2.30-1.20 (br, $CH+CH_2$), $M_{n\ SEC}$ = 14000 g/mol; M_w/M_n = 1.18.

2.3. Preparation of PS-CoNPs using Carboxylic acid End-Functionalized Polystyrene (PS-COOH)

2.3.1. Preparation of PS-CoNPs on 1.8 g scale

To a 100 mL three necked round bottom flask equipped with condenser, stir bar and thermocouple was added a solution of carboxylic acid end-functionalized polystyrene (PS-COOH, 0.80 g, 6.7×10^{-2} mmol) in 1,2-dichlorobenzene (15 mL) and a solution of $Co_2(CO)_8$ (2.50 g, 7.3 mmol) in 1,2-dichlorobenzene (25 mL). The reaction mixture was heated at one of the target temperatures of 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, or 170 °C. Reaction time ranged from 1 hr to 6 hrs from temperature at 170 °C to 120 °C however reactions were allowed to run for 24 hrs without change in particle size or morphology. After cooling to room temperature, the ferrofluid was precipitated into stirring hexanes (800 mL) to yield a black precipitate, which was collected by sedimentation using a standard AlNiCo magnet and decanting of the hexanes phase. The resulting precipitate was dried *in vacuo* to yield a black powder (1.8 g), which was soluble in a variety of organic solvents (e.g., toluene, tetrahydrofuran and dichloromethane).

2.3.2. Preparation of PS-CoNPs on 7.6 g scale

The preparation of PS-CoNPs on 7.6 g scale was carried out by following the same procedure as described in section 2.3.1 with the exception of using PS-COOH (3.2 g, 2.7 x 10^{-1} mmol) and $Co_2(CO)_8$ (10.0 g, 29 mmol) in 1,2-dichlorobenzene (160 mL).

2.3.3. Preparation of PS-CoNPs on 19 g scale

The preparation of PS-CoNPs on 19 g scale was carried out by following the same procedure as described in section 2.3.1 with the exception of using PS-COOH (8.0 g, 6.7 x 10^{-1} mmol) and $Co_2(CO)_8$ (25.0 g, 73 mmol) in 1,2-dichlorobenzene (400 mL). It is important to note that at this scale mechanical stirring is essential to maintain optimal mixing of reaction mixture.

2.4. Kinetics of PS-CoNPs synthesis

To investigate the nucleation and growth process of nanoparticles in solution, we obtained transmission electron microscope (TEM) images of a series of aliquots drawn from the solution during the reaction at different reaction times and temperatures (Figure S8-10). A 0.1 mL aliquot drawn from the reaction was diluted with 3 mL of toluene, sonicated for 3 minutes and drop-casted onto a carbon coated copper grid at zero field.

2.5. Comparison of PS-COOH ligands and oleic acid ligands on the preparation of CoNPs

2.5.1. Synthesis of oleic acid coated CoNPs

The preparation of oleic acid coated CoNPs was carried out by following the same procedure as described for the PS-COOH coated experiment (section 2.3.1) with the exception of replacing PS-COOH ligand with oleic acid (19 mg, 6.7 x 10^{-2} mmol), which gave 0.68 g of irregular, flocculated Co particles (Figure S11A).

2.5.2. Synthesis of superparamagnetic oleic acid coated CoNPs

The preparation of superparamagnetic oleic acid coated CoNPs was carried out by following the same procedure as described for the PS-COOH coated experiment (section 2.3.1) with the exception of replacing PS-COOH ligand with oleic acid (0.8 g, 2.8 mmol), which resulted in the formation of uniformly sized superparamagnetic CoNPs (0.31 g, particle diameter = 14.0 ± 1.83 nm) (Figure S11B).

2.5.3. Synthesis of phenylethyl end-functionalized polystyrene coated CoNPs in the presence of oleic acid

The preparation of phenylethyl end-functionalized polystyrene coated CoNPs was conducted using the same procedure as previously described for the PS-COOH coated experiment (section 2.3.1) with the exception of using phenylethyl end-functionalized polystyrene (0.8 g, 5.7 x 10^{-2} mmol) and oleic acid (19 mg, 6.7 x 10^{-2} mmol), which gave an increased yield of nanoscopic superparamagnetic CoNPs along with larger particulate aggregates (Figure S11C).

2.5.4. Synthesis of phenylethyl end-functionalized polystyrene coated CoNPs

The preparation of phenylethyl end-functionalized polystyrene coated CoNPs was conducted using the same procedure as previously described for the PS-COOH coated experiment (section 2.3.1) with the exception of using phenylethyl end-functionalized polystyrene (0.8 g, 5.7 x 10^{-2} mmol), which afforded 0.75 g of micron sized particulates of metallic cobalt (Figure S11D).

3. Figures

Figure S1. Experimental setup for the preparation of PS-CoNPs

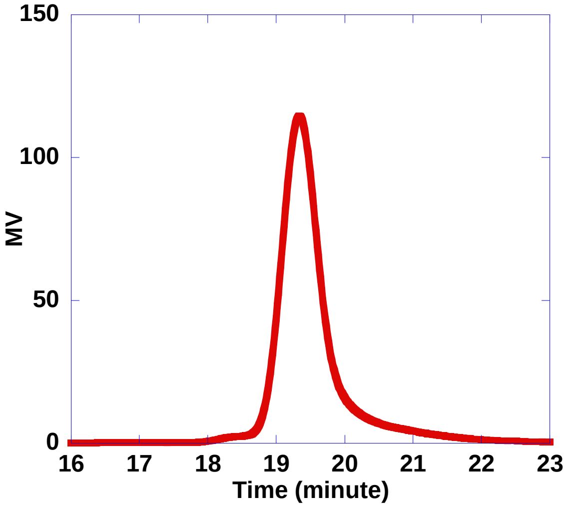

Figure S2. SEC trace of PS-COOH ($M_{n\ SEC}$ = 12000 g/mol, M_w/M_n = 1.11).

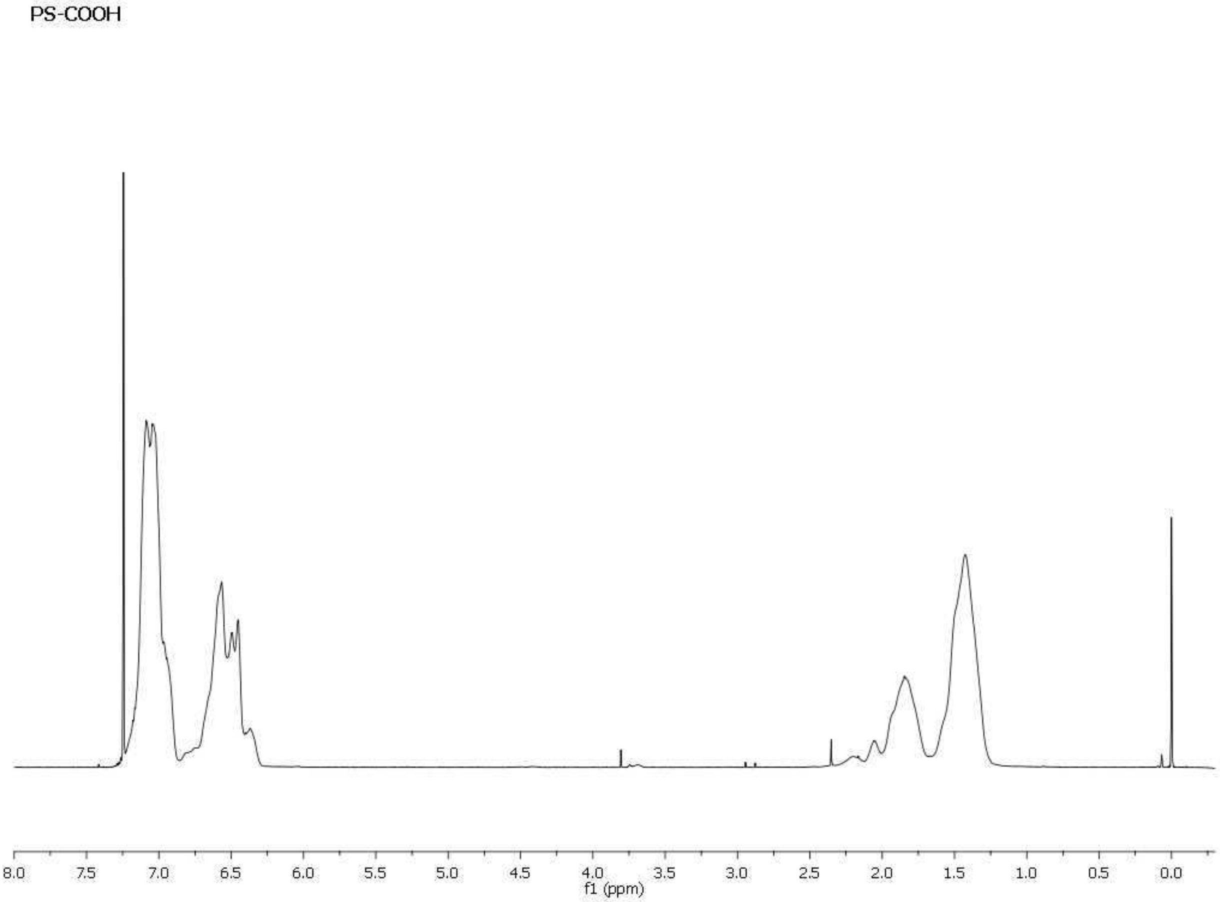

Figure S3. ^{1}H NMR spectrum of PS-COOH.

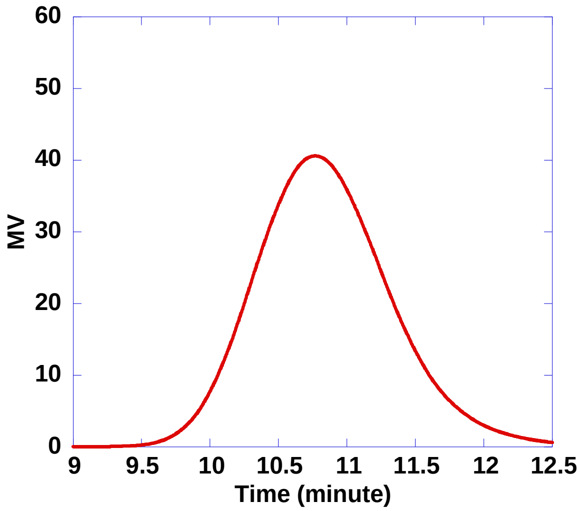

Figure S4. SEC trace of phenylethyl end-functionalized polystyrene ($M_{n\ SEC}$ = 14000 g/mol, M_w/M_n = 1.18).

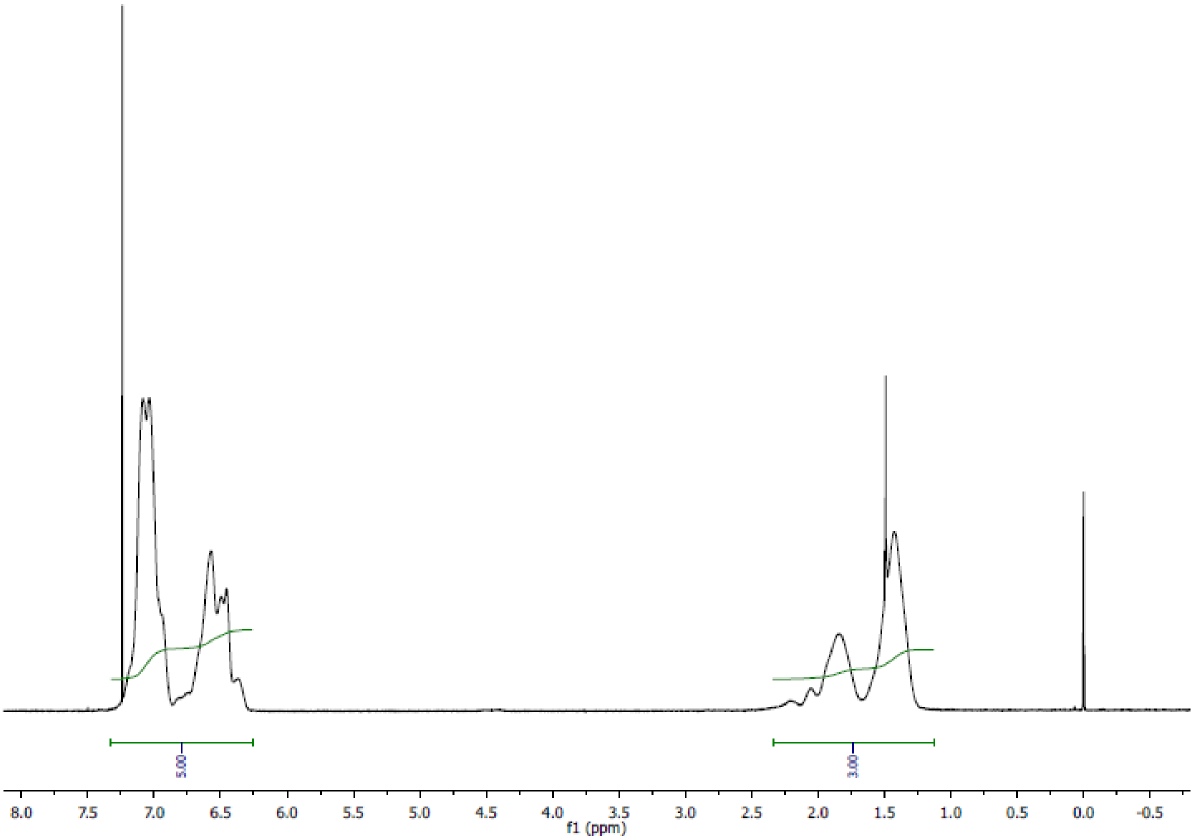

Figure S5. ^{1}H NMR spectrum of phenylethyl end-functionalized polystyrene

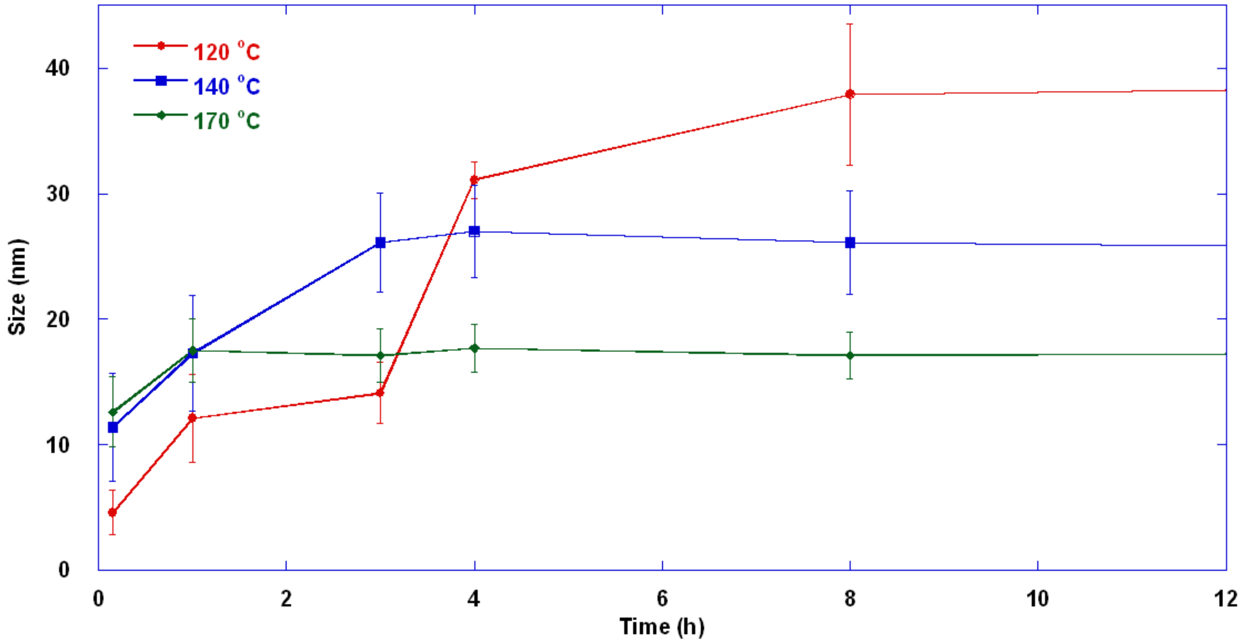

Figure S6. A plot of reaction time versus the average particle diameter formed at different reaction temperatures

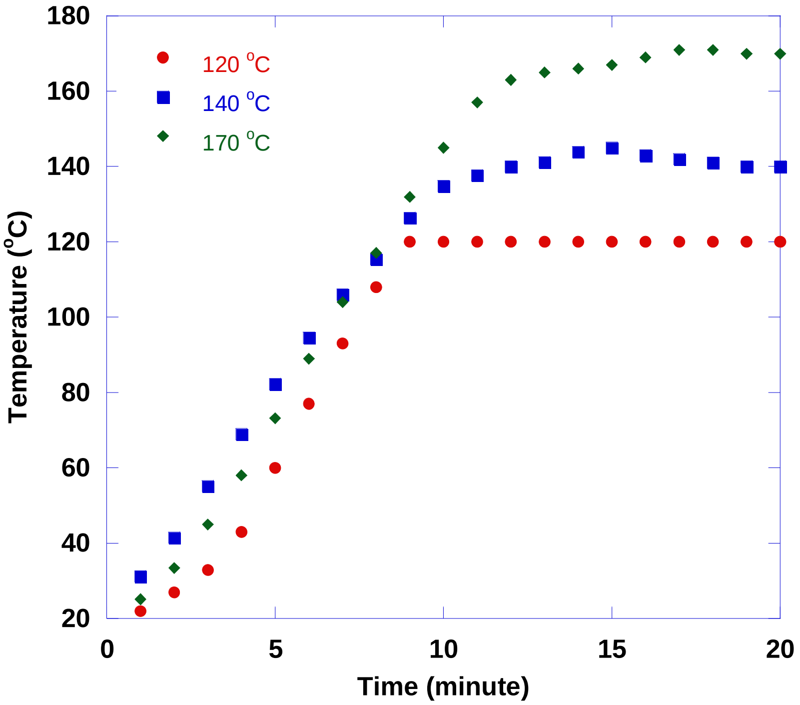

Figure S7. A plot of internal temperature versus the time of PS-CoNP reactions

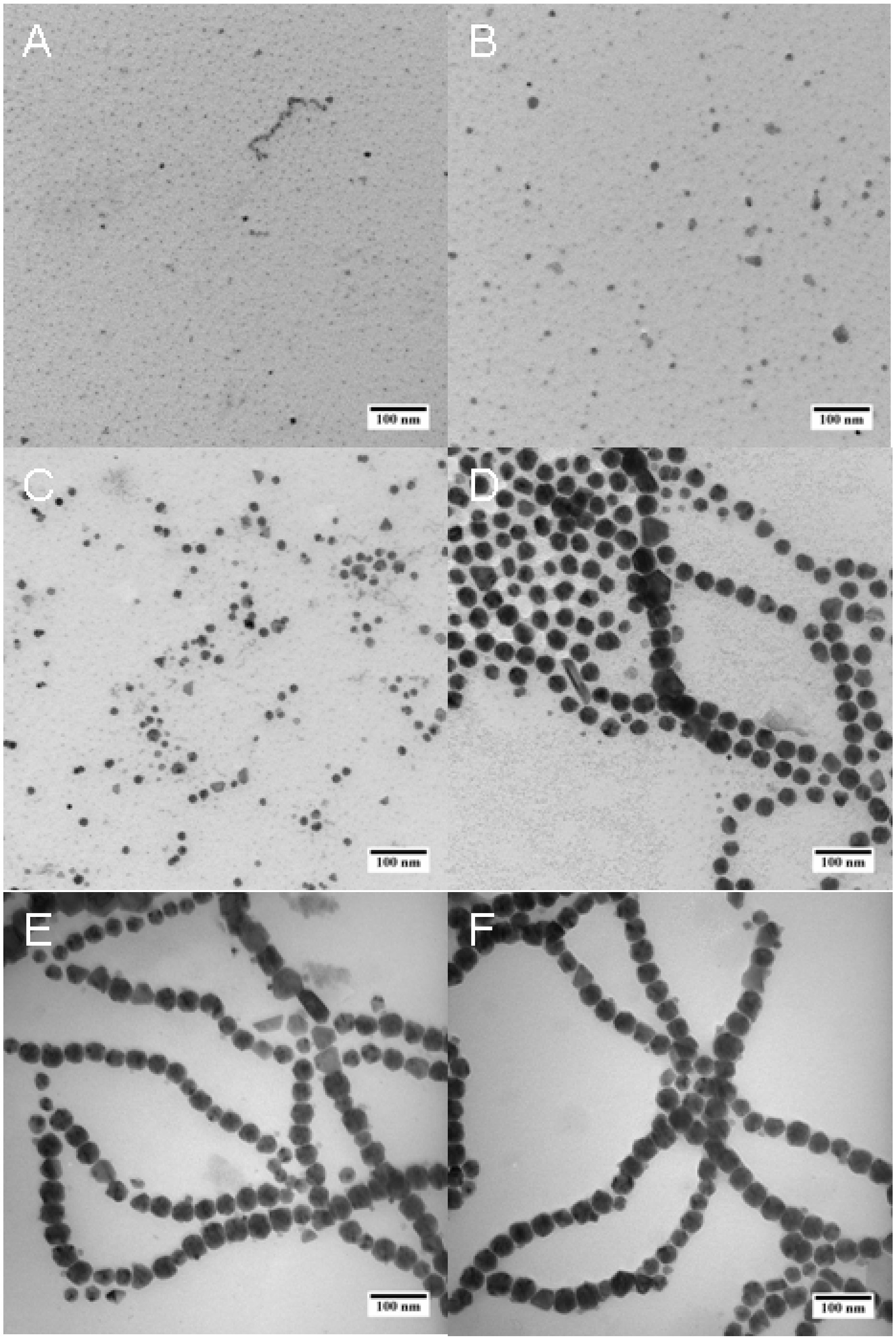

Figure S8. TEM images of PS-CoNPs in the sample aliquots drawn from solution at 120 °C at: (a) 15 min, with particle diameter = 4.60 ± 1.76 nm, (b) 1 h, with particle diameter = 12.1 ± 3.48 nm, (c) 3 h, with particle diameter = 14.1 ± 2.44 nm, (d) 4 h, with particle diameter = 31.1 ± 1.48 nm, (e) 8 h, with particle diameter = 37.9 ± 5.64 nm, (f) 24 h, with particle diameter = 39.3 ± 3.66 nm.

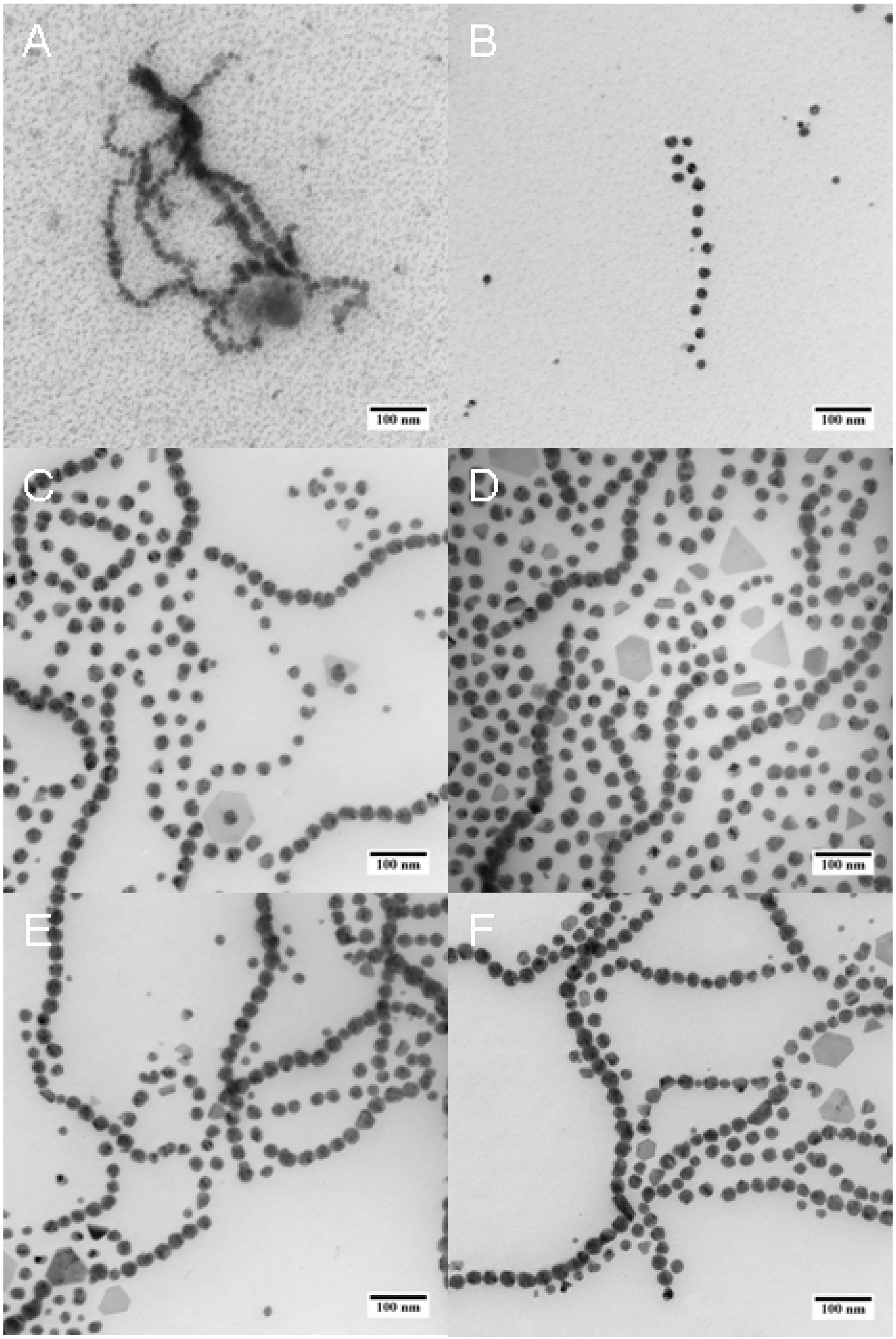

Figure S9. TEM images of PS-CoNPs in the sample aliquots drawn from solution at 140 °C at: (a) 15 min, with particle diameter = 11.4 ± 4.33 nm, (b) 1 h, with particle diameter = 17.3 ± 4.61 nm, (c) 3 h, with particle diameter = 26.1 ± 3.97 nm, (d) 4 h, with particle diameter = 27.0 ± 3.66 nm, (e) 8 h, with particle diameter = 26.1 ± 4.10 nm, (f) 24 h, with particle diameter = 24.9 ± 3.47 nm.

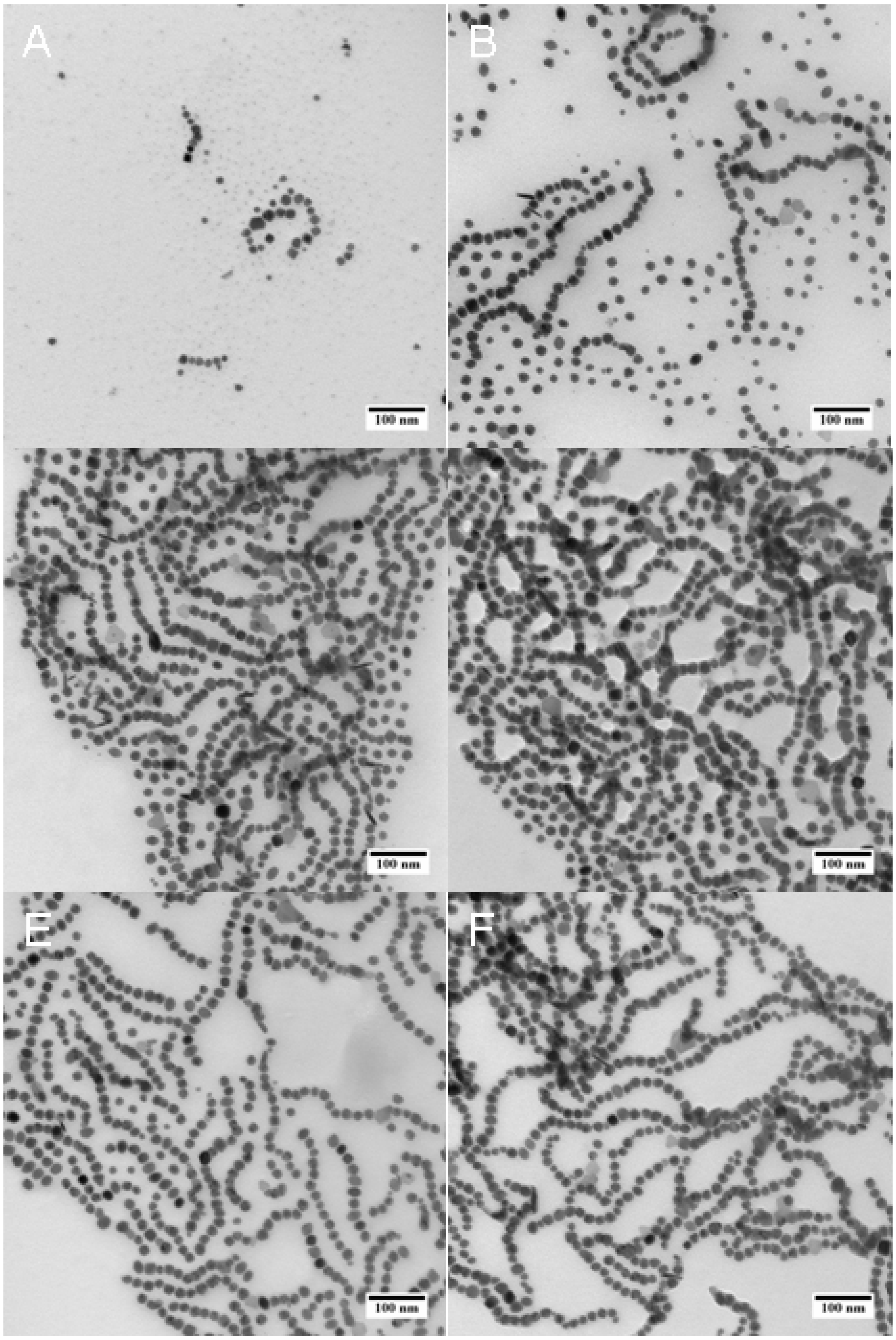

Figure S10. TEM images of PS-CoNPs in the sample aliquots drawn from solution at 170 °C at: (a) 15 min, with particle diameter = 12.6 ± 2.79 nm (b) 1 h, with particle diameter = 17.5 ± 2.56 nm (c) 3 h, with particle diameter = 17.1 ± 2.17 nm, (d) 4 h, with particle diameter = 17.7 ± 1.93 nm, (e) 8 h, with particle diameter = 17.1 ± 1.84 nm, (f) 24 h, with particle diameter = 17.6 ± 2.39 nm.

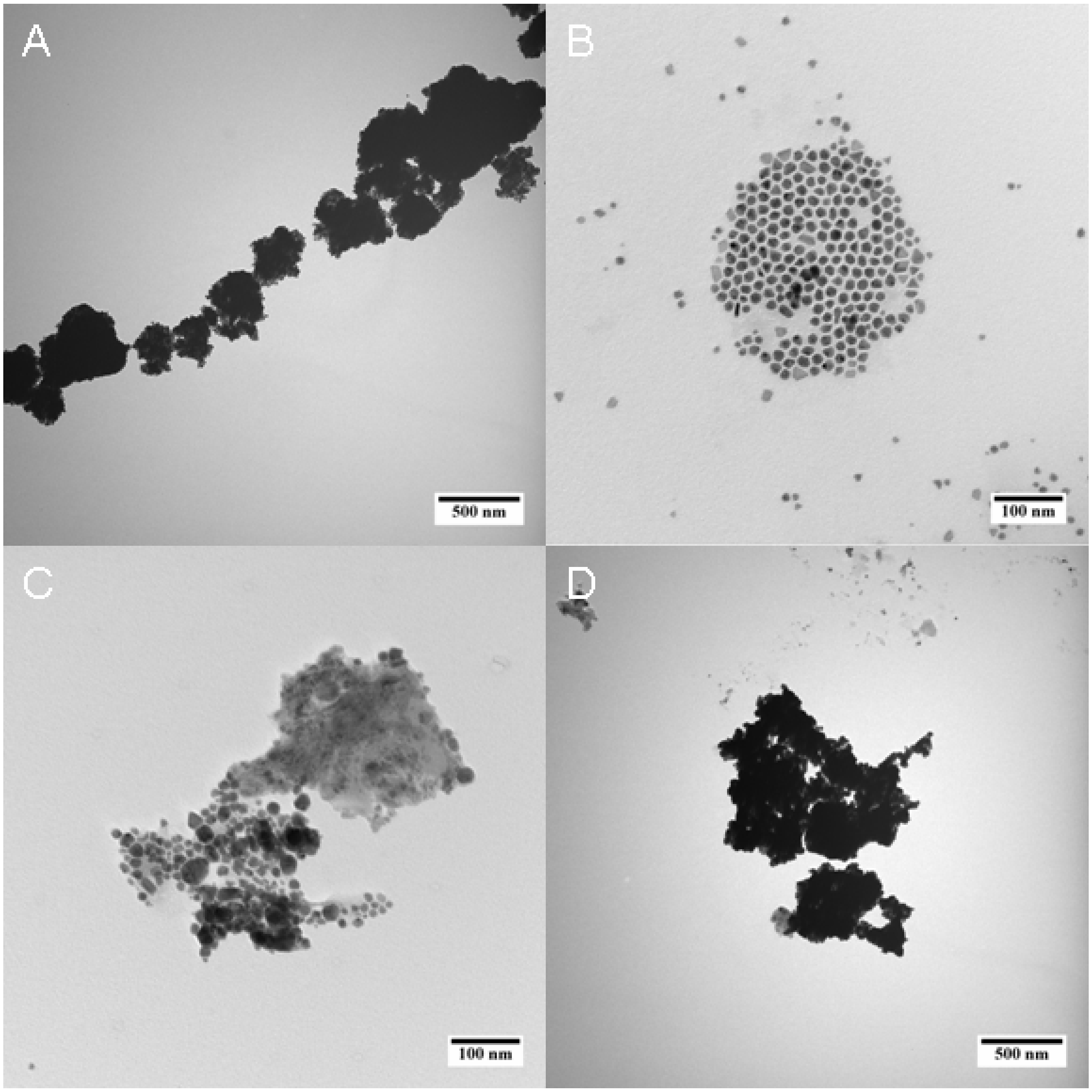

Figure S11. TEM images of CoNPs in the sample aliquots drawn from solution under different reaction conditions: (a) 6.67 x 10^{-2} mmol of oleic acid (section 2.5.1), (b) 0.8 g of oleic acid, with particle diameter = 14.0 ± 1.83 nm (section 2.5.2), (c) 6.67 x 10^{-2} mmol of oleic acid and 0.8 g of phenylethyl end-functionalized polystyrene (section 2.5.3), (d) 0.8 g of phenylethyl end-functionalized polystyrene (section 2.5.4).

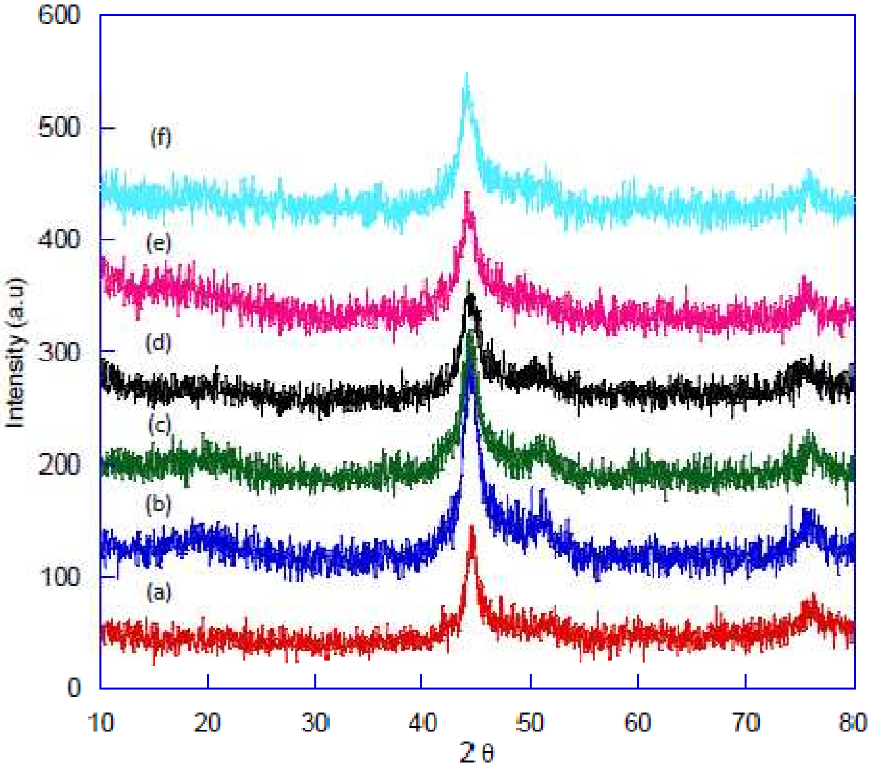

Figure S12. Overlay XRD patterns of PS-CoNPs prepared at different temperature (a) 120 °C, D = 43 ± 5.4 nm, (b) 130 °C, D = 35 ± 3.9 nm, (c) 140 °C, D = 28 ± 4.6 nm, (d) 150 °C, D = 25 ± 3.9 nm, (e) 160 °C, D = 23 ± 3.5 nm, (f) 170 °C, D = 18 ± 2.4 nm.

Powder X-ray diffraction (XRD) was used to characterize the solid-state structure of PS-CoNPs. The XRD results confirmed that PS-CoNPs in all cases exhibited a metallic face-centered cubic (fcc) cobalt phase possessing low degrees of crystallinity. The highest degree of crystallinity of PS-CoNPs formed at 120 °C correlated with the largest size of colloids formed at this temperature.

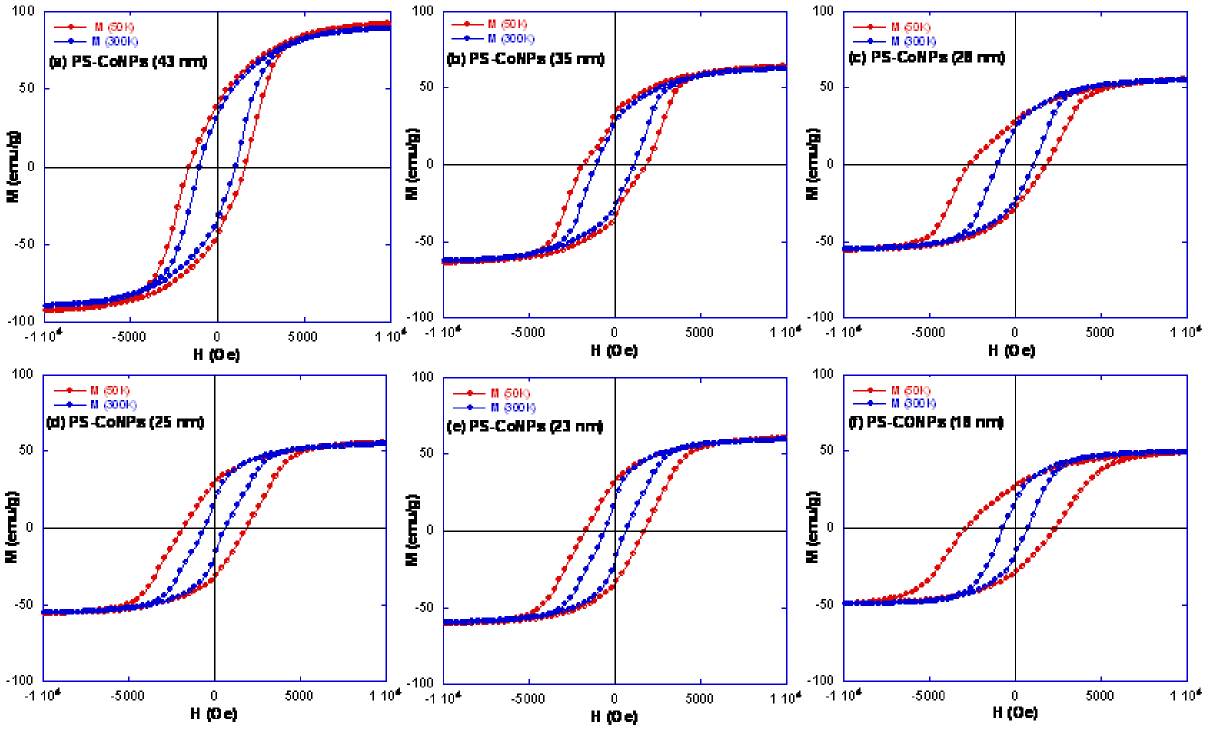

Figure S13. VSM of PS-CoNPs prepared at different temperature (a) 120 °C, D = 43 ± 5.4 nm, (b) 130 °C, D = 35 ± 3.9 nm, (c) 140 °C, D = 28 ± 4.6 nm, (d) 150 °C, D = 25 ± 3.9 nm, (e) 160 °C, D = 23 ± 3.5 nm, (f) 170 °C, D = 18 ± 2.4 nm.

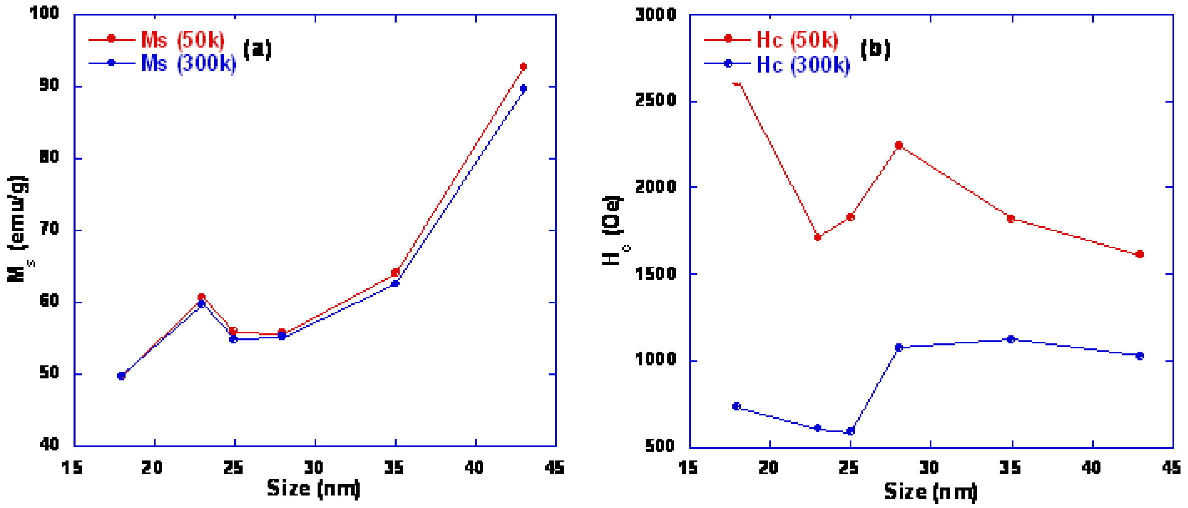

Figure S14. Plots of the particle diameter of PS-CoNPs versus (a) saturation magnetization (M_s), (b) magnetic coercivity (H_c)

4. Reference

(1) Keng Pei, Y.; Shim, I.; Korth Bryan D.; Douglas Jack, F.; Pyun, J. *ACS Nano* **2007**, *1*, 279