

Synthesis of ferromagnetic polymer coated nanoparticles on multi-gram scale with tunable particle size†

Mathew M. Bull,^a Woo Jin Chung,^a Sarah R. Anderson,^a Su-jeong Kim,^b In-Bo Shim,^c Hyun-jong Paik^b and Jeffrey Pyun^{*ad}

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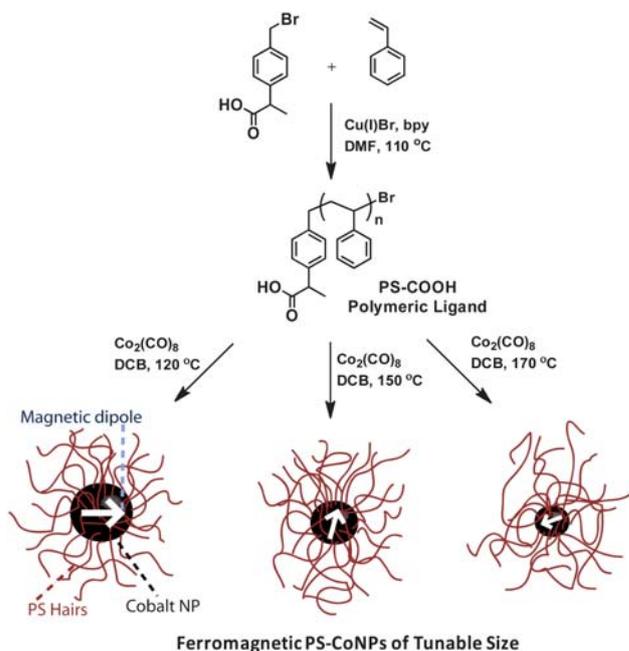
The synthesis of ferromagnetic cobalt nanoparticles with polymeric ligands with tunable particle size is reported on multi-gram scales. End-functional polystyrene ligands were prepared via atom transfer radical polymerization. Mechanistic studies on this system were conducted as well as direct comparisons of polymer vs. small molecule ligand effects on nanoparticle formation.

The preparation of magnetic nanoparticles has been investigated for a wide range of applications in biotechnology, information storage and catalysis.¹ Despite these advances, the development of robust synthetic methods to prepare well-defined magnetic nanoparticles (NPs) in gram-scale quantities remains an important challenge. Two general approaches, termed “hot injection,” or “heat-up” methods have been developed to prepare magnetic nanoparticles.² The vast majority of synthetic methods have focused on hot injection methods to prepare superparamagnetic NPs and are limited to sub-gram quantities. The elegant system of Hyeon *et al.* is a notable exception where uniform superparamagnetic magnetite (Fe₃O₄) NPs were prepared in 40 g batches using a one-pot, “heat-up” method.^{2e}

The synthesis of ferromagnetic NPs has gained attention to prepare self-assembled one-dimensional (1-D) mesostructures.³ While the preparation of superparamagnetic NPs has been widely investigated, the synthesis of well-defined ferromagnetic NPs, particularly in gram-quantities, has not been as extensively explored. The preparation of ferromagnetic iron (Fe) NPs has been conducted using either polystyrenic or polyisobutylene based copolymers on over 50 g scales per batch.⁴ However, due to the rapid oxidation of FeNPs, the preparation of both ferrimagnetic Fe₃O₄ and ferromagnetic cobalt nanoparticles (CoNPs) has also been pursued.³ Recently, our group has developed a hot injection method to prepare ferromagnetic CoNPs using end-functional polystyrene ligands on one to two gram scales.^{3k,l} However, attempts to synthesize multi-gram quantities of

uniform ferromagnetic CoNPs from this approach were unsuccessful due to logistical challenges of delivering large quantities of the metal precursor (Co₂(CO)₈) and maintaining identical heating profiles as observed in the smaller scale system.

Herein, we report a novel, versatile synthesis of ferromagnetic polymer coated cobalt NPs which afforded multi-gram quantities per batch and also allows for systematic variation of particle size (Scheme 1). To our knowledge this report is the first study to controllably tune the particle size of larger ferromagnetic CoNPs and is the first mechanistic report to unify the different reaction conditions (*i.e.*, high vs. low temperature, small molecule vs. polymeric ligands) used to prepare these colloids. Extensive reports using small molecule ligands (*e.g.*, oleic acid and trioctylphosphine oxide) have demonstrated the ability to form uniform superparamagnetic CoNPs (particle size < 10 nm).^{2h,3e} Conversely, the use of (co)polymeric ligands in toluene at *T* = 110 °C has been demonstrated to form ferromagnetic CoNPs (particle size > 10 nm).³ Both of these types of systems exhibit some control of particle size to obtain both superparamagnetic and ferromagnetic CoNPs by variation of ligand to NP precursor feed ratios at a single reaction temperature. However, this report is the first demonstration to prepare well-defined



Scheme 1 Synthetic scheme for the preparation of PS-ligands and ferromagnetic PS-coated cobalt nanoparticles.

^aDepartment of Chemistry and Biochemistry, University of Arizona, 1306 E. University Blvd., Tucson, AZ, 85721, USA. E-mail: jpyun@email.arizona.edu; Fax: +1 520-621-8407; Tel: +1 520-626-1834

^bDept. Polymer Science & Engineering, Pusan National University, San 30 Jangjundong Kumjunggu, Busan, 609-735, South Korea. E-mail: hpaik@pusan.ac.kr; Fax: +82 51 513 7720; Tel: +82 51 510 2402

^cDepartment of Nano and Electronic Physics, Kookmin University, Seoul, 136-702, South Korea. E-mail: ibshim@kookmin.ac.kr; Fax: +82-2-910-5170; Tel: +82-2-910-4757

^dWorld Class University Program for Chemical Convergence for Energy & Environment, Department of Chemical & Biological Engineering, Seoul National University, Seoul, 151-744, South Korea

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ferromagnetic CoNPs over a wide temperature range with a ligand system that incorporated attributes of both small molecules and polymers. Colloids made from this approach were passivated with carboxylic acid terminated PS ligands (PS-COOH), which imparted excellent colloidal stability to dispersed NPs. Furthermore, the polymer coating enabled both isolation of NPs in powder form and facile redispersion of colloids in organic solvents (*e.g.*, THF and toluene).

The general synthetic investigation that was conducted involved the preparation of PS-COOH ligands *via* atom transfer radical polymerization (ATRP),⁵ followed by examination of temperature effects to form CoNPs of varying size. In our earlier hot injection method, amine (NH₂) end-functional PS ligands were observed to afford the most optimal forms of ferromagnetic PS-CoNPs. However, using these one-pot conditions, the use of PS-COOH and PS-terminated phosphonic acid ligands was found to be viable. The use of PS-COOH ligands was focused on in this study due to the synthetic accessibility of this material in a one-step synthesis *via* the ATRP of styrene from a commercially available initiator, 2-[4-(bromomethyl)phenyl]propanoic acid. PS-COOH of low polydispersity over a molecular weight range of 5000 to 30 000 g mol⁻¹ was prepared and evaluated in the formation of ferromagnetic PS-CoNPs, but dependence of molecular weight on PS-CoNP synthesis was not observed. Hence, for practical and economic use of the initiator (*i.e.*, higher MW's require less initiator), molar masses in the range of 10 000 to 20 000 were used and evaluated in this study.

Ferromagnetic PS-CoNPs were prepared by the thermolysis of Co₂(CO)₈ (1.8 × 10⁻¹ M) in the presence of PS-COOH (1.7 × 10⁻³ M) ligands in 1,2-dichlorobenzene (DCB). A surprising feature of this system was the ability to tune the particles size of PS-CoNPs over a range of 18 to 43 nm using the same feed ratios of PS-COOH to Co₂(CO)₈ with simple variation of reaction temperature. A temperature range of 120 to 170 °C was chosen to comprehensively study the effect of reaction temperature on size using the same ligand system. Reactions conditions at *T* = 170, 160, 150, 140, 130 and 120 °C afforded ferromagnetic PS-CoNPs with diameters of 18 ± 2.4 nm, 23 ± 3.5 nm, 25 ± 3.9 nm, 28 ± 4.6 nm, 35 ± 3.9 nm and 43 ± 5.4 nm, respectively, as determined from TEM (Fig. 1). The formation of mesoscopic NP chains was also confirmed by TEM for all of these samples, which arose from dipolar associations between PS-CoNPs.

A striking linear correlation of thermolysis temperature with PS-CoNP particle size was observed over a range from 120 °C to 170 °C for reactions in DCB (Fig. 2). Particle reactions below 120 °C afforded PS-CoNPs possessing a broad size distribution with a mixture of superparamagnetic and ferromagnetic colloids. A reaction temperature of 170 °C was the upper limit for experiments conducted in DCB, however, switching solvents to 1,3,5-trichlorobenzene (TCB) enabled evaluation of PS-CoNP synthesis at 200 °C, which afforded colloids with diameters of 14 ± 2 nm and fitted to the linear trend of particle size *vs.* reaction temperature. This new one-pot method was also employed to scale up the synthesis of ferromagnetic PS-CoNPs to multi-gram quantities per batch. The initial scale that was examined for this system utilized a total volume of 40 mL of DCB, 0.80 g of PS-COOH and 2.5 g of Co₂(CO)₈ at 140 °C, which afforded an isolated yield of 1.8 g after precipitation. This reaction condition was easily scaled up by a factor of 4× and 10×, which afforded isolated yields of 7.6 g and 19 g, respectively. In principle, this process could be utilized to prepare PS-CoNPs in

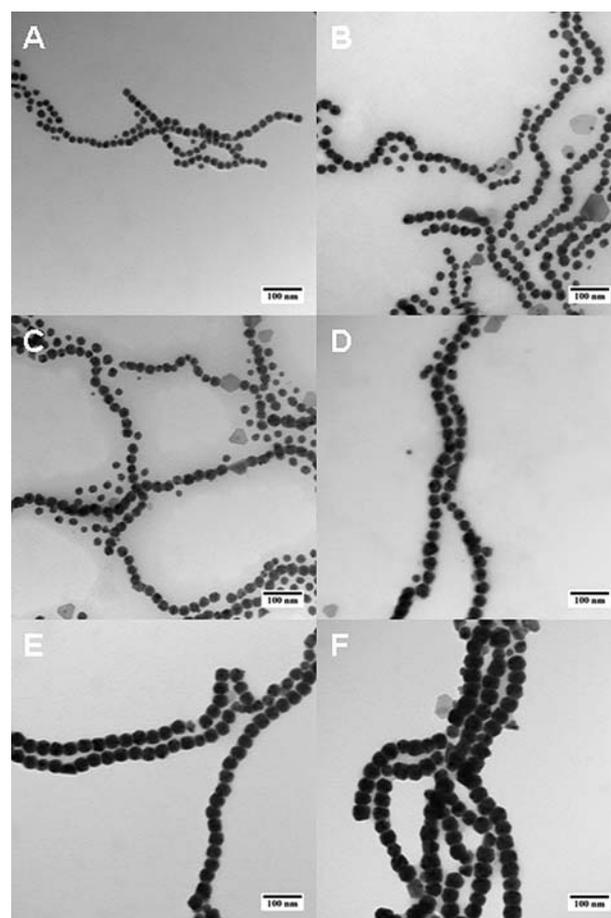


Fig. 1 TEM micrographs showing the range of PS-CoNP sizes produced at different temperatures during the thermolysis reaction of Co₂(CO)₈ with the presence of PS-COOH surfactant in 1,2-DCB as shown in Scheme 1. (A) At 170 °C, *D* = 18 ± 2.4 nm, (B) at 160 °C, *D* = 23 ± 3.5 nm, (C) at 150 °C, *D* = 25 ± 3.9 nm, (D) at 140 °C, *D* = 28 ± 4.6 nm, (E) at 130 °C, *D* = 35 ± 3.9 nm and (F) at 120 °C, *D* = 43 ± 5.4 nm PS-CoNPs were cast onto supporting surfaces from a particle dispersion in toluene.

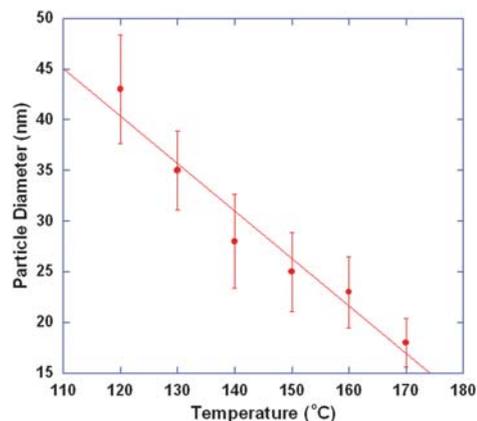


Fig. 2 A plot of reaction temperature during the thermolysis reaction of Co₂(CO)₈ in the presence of PS-COOH ligands *versus* the average particle diameter formed in each reaction.

larger quantities, but practical apparatus constraints limited the scale demonstrated in this report. It is also important to note that thermocouple fitted heating mantles were used, in comparison to thermostated oil baths. We observed major deviations of internal reaction mixture temperature *versus* external oil bath temperatures, which further lead to significant problems in the reproducibility of PS–CoNP synthesis.

A detailed kinetic investigation of PS–CoNP formation at $T = 170, 140$ and $120\text{ }^{\circ}\text{C}$ was conducted by correlation of particle size and morphology determined *via* TEM (see ESI†, Fig. S6–S10). The heating profile for these experiments indicated that the internal target temperatures were reached within 12 min at $T = 120, 140$ and $170\text{ }^{\circ}\text{C}$, respectively. Conversely, the reaction time necessary to reach final particle sizes at $T = 120, 140$ and $170\text{ }^{\circ}\text{C}$ required 6 h, 3 h and 1 h, which confirmed that PS–CoNP growth extended significantly beyond the initial thermal equilibration period (see ESI†, Fig. S6 and S7). Despite variation of temperatures, the formation of small CoNPs that coalesced into larger, nearly uniform colloids was observed, indicative of Ostwald ripening. Furthermore, the systematic variation of particle size was attributed to a kinetically controlled process, as higher reaction temperature promoted faster dissolution and nucleation of metal carbonyl precursors into growing CoNPs.[†]

One of the key fundamental questions from this system was the role of the polymer in the formation and stabilization of PS–CoNPs. Direct comparisons of CoNP synthesis using oleic acid *vs.* PS–COOH revealed that the PS backbone (in addition to the COOH group) weakly interacted with Co surfaces (see ESI†, Fig. S11). Experiments typically performed at $140\text{ }^{\circ}\text{C}$ with PS–COOH ligands (at $1.75 \times 10^{-3}\text{ M}$ in DCB) afforded well-defined ferromagnetic CoNPs, as previously discussed. However, when oleic acid ligands were used at similar concentrations ($1.7 \times 10^{-3}\text{ M}$) the formation of irregular, flocculated Co particulates was observed. The addition of free phenylethyl terminated PS as a control polymer (at $1.4 \times 10^{-3}\text{ M}$) and oleic acid (at $1.7 \times 10^{-3}\text{ M}$) was observed to increase the yield of nanoscopic superparamagnetic CoNPs, along with larger particulate aggregates. At much higher feed ratios of oleic acid ($7 \times 10^{-2}\text{ M}$), the formation of uniformly sized superparamagnetic CoNPs was observed.

These results indicated that PS itself interacted with CoNP surfaces and imparted some degree of colloidal stabilization, which has been observed in related systems through association of Co sites with electron rich phenyl side chain groups.⁶ However, the use of a ligand terminated PS (*e.g.*, amines, COOH, phosphonic acids) was observed to be necessary for the preparation of well-defined ferromagnetic CoNPs, as phenylethyl terminated PS (*i.e.* PS without COOH end-group) alone only afforded micron sized particulates of metallic cobalt, which readily flocculated from DCB (see ESI†, Fig. S11D). Thus, it is both the incorporation of the ligating COOH end-group and the weakly associating PS backbone into a single macromolecule that synergistically promoted the formation of ferromagnetic CoNPs.

Solid state characterization of PS–CoNPs prepared at different temperatures confirmed the preparation of ferromagnetic colloids as determined using powder X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). In all cases, XRD confirmed the formation of metallic face-centered cubic (fcc) cobalt possessing low degrees of crystallinity (see ESI†, Fig. S12). VSM also confirmed that all samples formed over the range of $120\text{ }^{\circ}\text{C}$ to $170\text{ }^{\circ}\text{C}$ were ferromagnetic at 50 K and 300 K. We observed a progressive increase of saturation magnetization (M_s) with increasing size of PS–CoNPs over

a range of $40\text{--}90\text{ emu g}^{-1}$, which were essentially identical at 50 K and 300 K (see ESI†, Fig. S14). Conversely, the magnetic coercivity (H_c) at 50 K was observed to decrease with increasing particle size, which was indicative of multi-domain behavior with PS–CoNPs. The behavior of H_c at 300 K of PS–CoNPs was significantly lower than at 50 K due to the contributions of thermal fluctuations, however, a stable $H_c \approx 1000\text{ Oe}$ was observed for PS–CoNPs above 28 nm in diameter. For PS–CoNPs in the range of $18\text{--}26\text{ nm}$ in size, coercivities in the range of $586\text{--}730\text{ Oe}$ were observed *via* VSM at 300 K (see ESI†, Fig. S14B).

In conclusion, a robust one-pot method to prepare ferromagnetic PS–CoNPs is reported. This system enabled the control of the size of PS–CoNPs by simple variation of temperature and further demonstrated the ability to prepare multi-gram quantities of these materials.

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Notes and references

- (a) T. Hyeon, *Chem. Commun.*, 2003, 927–934; (b) M. Green, *Chem. Commun.*, 2005, 3002–3011; (c) Y.-W. Jun, J.-S. Choi and J. Cheon, *Chem. Commun.*, 2007, 1203–1214; (d) S. Sun, *Adv. Mater.*, 2006, **18**, 393–403; (e) R. B. Grubbs, *Polym. Rev.*, 2007, **47**, 197–215; (f) J. Park, J. Joo, S. G. Kwon, Y. Jang and T. Hyeon, *Angew. Chem., Int. Ed.*, 2007, **46**, 4630–4660; (g) J. Pyun, *Polym. Rev.*, 2007, **47**, 231–263.
- (a) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715; (b) X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343–5344; (c) S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989–1992; (d) T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798–12801; (e) J. Park, E. Lee, N. M. Hwang, M. Kang, S. C. Kim, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park and T. Hyeon, *Angew. Chem., Int. Ed.*, 2005, **44**, 2872–2877; (f) S. G. Kwon, Y. Piao, J. Park, S. Angappane, Y. Jo, N. M. Hwang, J. G. Park and T. Hyeon, *J. Am. Chem. Soc.*, 2007, **129**, 12571–12584; (g) J. Park, K. An, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, **3**, 891–895; (h) S. Sun and C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325–4330.
- (a) D. Kim, N. Lee, M. Park, B.-H. Kim, K. An and T. Hyeon, *J. Am. Chem. Soc.*, 2009, **131**, 454–455; (b) J. R. Thomas, *J. Appl. Phys.*, 1966, **37**, 2914–2915; (c) C. H. Griffiths, M. P. O'Horo and T. W. Smith, *J. Appl. Phys.*, 1979, **50**, 7108–7115; (d) O. A. Platonova, L. M. Bronstein, S. P. Solodovnikov, I. M. Yanovskaya, E. S. Obolonkova, P. M. Valetsky, E. Wenz and M. Antonietti, *Colloid Polym. Sci.*, 1997, **275**, 426–431; (e) V. F. Puentes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115–2117; (f) S. L. Tripp, S. V. Puzstay, A. E. Ribbe and A. Wei, *J. Am. Chem. Soc.*, 2002, **124**, 7914–7915; (g) F. S. Diana, S.-H. Lee, P. M. Petroff and E. J. Kramer, *Nano Lett.*, 2003, **3**, 891–895; (h) G. J. Liu, X. H. Yan, C. Curda and J. Lal, *Chem. Mater.*, 2005, **17**, 4985–4991; (i) G. Cheng, D. Romero, G. T. Fraser and A. R. High Walker, *Langmuir*, 2005, **21**, 12055–12059; (j) J. Gao, B. Zhang, X. Zhang and B. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 1220–1223; (k) B. D. Korth, P. Keng, I. Shim, S. E. Bowles, C. Tang, T. Kowalewski, K. W. Nebesny and J. Pyun, *J. Am. Chem. Soc.*, 2006, **128**, 6562–6563; (l) P. Y. Keng, I. Shim, B. D. Korth, J. F. Douglas and J. Pyun, *ACS Nano*, 2007, **1**(4), 279–292.
- N. A. D. Burke, H. D. H. Stöver and F. R. Dawson, *Chem. Mater.*, 2002, **14**, 4752–4761.
- K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
- K. David, N. Dan and R. Tannenbaum, *Surf. Sci.*, 2007, **601**, 1781–1788.