### Supplementary Information

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## Self-Assembly of Well-Defined Ferrocene Triblock Copolymers and Their Template Synthesis of Ordered Iron Oxide Nanoparticles

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#### **Experimental Section**

#### Materials

All reagents were purchased from Alfa Aesar and Aldrich and used as received unless otherwise noted. 2-(Methacryloyloxy)ethyl ferrocenecarboxylate (MAEFc) and ATRP macroinitiator PEO-Br were prepared according to reported procedures.<sup>1,2</sup> Styrene was distilled before use. AIBN was recrystallized from diethyl ether before use.

#### Characterization

<sup>1</sup>H NMR (300 MHz) spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. GPC was performed at 50°C on a Varian

system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1, HR2 ( $300 \times 7.5$  mm) from Waters. HPLC grade DMF was used as eluent with 0.01 wt% LiBr at a flow rate of 0.8 mL/min. Polystyrene standards were used for calibration. Atomic force microscopy (AFM) was conducted on a Nanoscope V Multimode instrument, operating under tapping mode. 1.5 weight % solutions of the block copolymers in toluene were spin-coated onto cleaned silicon wafers. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K<sup>+</sup> source. The energy scale of the system was calibrated using Au foil with Au4f scanned for the Al radiation and Cu foil with Cu2p scanned for Mg radiation resulting in a difference of  $1081.70 \pm 0.025$  eV between these two peaks. The binding energy was calibrated using an Ag foil with Ag3d5/2 set at  $368.21 \pm 0.025$  eV for the monochromatic Al X-ray source. The monochromatic Al K<sup>+</sup> source was operated at 15 keV and 120 W. The pass energy was fixed at 40 eV for the detailed scans. A charge neutralizer (CN) was used to compensate for the surface charge. Samples were not conductive and C1s was used as the peak reference. The binding energy (BE eV) was corrected with the C1s (284.6 eV) as standard. X-ray diffraction (XRD) measurements were conducted on a Rigaku D/Max 2100 Powder X-Ray Diffractometer (Cu K<sup>+</sup> radiation) instrument and scanned from 10° to 85° with a step size of 0.005° and a step rate of 6 s.

# Synthesis of diblock copolymer Poly(ethylene oxide)-*b*-poly(2-(methacryloyloxy)ethyl ferrocenecarboxylate) (PEO-*b*-PMAEFc-Br)

PEO-Br (1.00 g, 0.20 mmol), MAEFc (4.12 g, 12.01 mmol), Cu(I)Br (34.3 mg, 0.23 mmol), bpy (75.0 mg, 0.48 mmol) were added to a to a 50-mL Schlenk flask and degassed by

purging with nitrogen. Distilled toluene (20 mL) was added to a 50 mL round bottom flask and degassed by bubbling the solution with nitrogen gas for 30 min. The toluene was then transferred to the schlenk line flask and the mixture was further degassed by nitrogen bubbling for 5 min. The reaction was stirred at room temperature for 15 min before the flask was placed in an oil bath preheated to 90 °C. An initial sample was taken in order to accurately determine the reaction conversion by <sup>1</sup>H NMR. Samples were periodically taken over the course of the polymerization to determine percent conversion by <sup>1</sup>H NMR. The polymerization was quenched when it reached 40% conversion by placing the Schlenk flask in an ice bath. The mixture was diluted with THF and passed through a short neutral alumina plug, concentrated, precipitated into diethyl ether three times and vacuum dried at room temperature overnight. The degree of polymerization was determined to be 25 by <sup>1</sup>H NMR analysis. MW<sub>PMAEFc</sub>=8300. MW<sub>PEO-b-PMAEFc</sub>=13300. Yield = 2.3 g. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (TMS, ppm): 4.19-4.82 (m, 325 H, C<sub>5</sub>H<sub>5</sub>-Fe-C<sub>5</sub>H<sub>4</sub>-C(=O)OCH<sub>2</sub>CH<sub>2</sub>), 3.63 (s, 452 H, -OCH<sub>2</sub>CH<sub>2</sub>-), 0.8-2.2 (m, 75 H, -CH<sub>2</sub>-C(CH<sub>3</sub>)). GPC: Mn = 12600, PDI = 1.17.

Poly(ethyleneoxide)-b-poly(2-(methacryloyloxy)ethylferrocenecarboxylate)-b-poly(styrene)(PEO-b-PMAEFc-b-PS)by ATRP.PEO-b-PMAEFc-Br (1 eq.) and Cu(I)Br(0.1 eq) were placed in a 10 mL schlenk line flask and purged with nitrogen for 20 minutes.Styrene (s eq.), PMDETA (1.2 eq), and 2 mL toluene were added to a 5 mL pearl shaped flaskand degassed nitrogen bubbling for 20 minutes.The monomer, ligand, and solvent were thentransferred to the schlenk line flask and further degassed by nitrogen bubbling for 5 minutes.The reaction was stirred at room temperature for 15 min before the flask was placed in an oilbath preheated to 90 °C.An initial sample was taken in order to accurately determine the

reaction conversion by <sup>1</sup>H NMR. Samples were periodically taken over the course of the polymerization to determine percent conversion by <sup>1</sup>H NMR. The polymerization was quenched when it reached 80% conversion by placing the Schlenk flask in an ice bath. The mixture was precipitated into methanol three times and vacuum dried at room temperature overnight. The degree of polymerization was determined by <sup>1</sup>H NMR analysis. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (TMS, ppm): 6.30-7.20 (m, PS Ph), (4.19-4.82 (m, C<sub>5</sub>H<sub>5</sub>-Fe-C<sub>5</sub>H<sub>4</sub>-C(=O)OCH<sub>2</sub>CH<sub>2</sub>), 3.63 (s, -OCH<sub>2</sub>CH<sub>2</sub>-), 0.8-2.2 (m, PMAEFc CH<sub>2</sub>C(CH<sub>3</sub>) and PS CH<sub>2</sub>-CH).

#### **Preparation of Thin Films**

The triblock copolymers were spin coated from 1.5wt% toluene solution onto silicon wafer substrates. The thin films were then solvent annealed under controlled humidity as reported earlier.<sup>3,4</sup> The films were annealed for 12h under saturated toluene vapor supplied by a neighboring solvent reservoir in a sealed chamber. After the solvent annealing process, selected films were treated by UV/Ozonolysis for 2 h and further pyrolysis at 1200 °C for 20 min.



**Figure S1**. <sup>1</sup>H NMR spectra for diblock copolymer PEO-*b*-PMAEFc-Br and triblock copolymer PEO-*b*-PMAEFc-*b*-PS.

Polymer	M (PS) $\sigma/mol^a$	M (total) $\sigma/mol^a$	Wt% PS	PDIp	Mornhology
rorymen	$M_n$ (1.5), g/mor	$M_n$ (total), g/mor	WU/015	I DI	wiorphology
2.	12100	25400	17 60/	1 42	Disandanad
3a	12100	25400	4/.0%	1.42	Disordered
3h	56000	69300	80.8%	1 39	Cylindrical
50	20000	07500	00.070	1.59	Cymarical
20	02600	105000	07 /0/	1.50	Disordarad
50	92000	103900	0/.470	1.39	Disordered

 Table S1.
 Characterization for triblock copolymers 3a-3c.

<sup>a</sup>Determined from <sup>1</sup>H NMR.

<sup>b</sup>Determined from GPC.



Figure S2. AFM image (height) of triblock copolymer 3a.



Figure S3. AFM image (height) of triblock copolymer 3c.



**Figure S4**. XPS spectrum of iron oxide nanoparticles after UV/O and pyrolysis of triblock copolymer PEO-*b*-PMAEFc-*b*-PS (**3b**).

 Table S2. XRD comparison (peak positions in degree) between our iron oxide nanoparticles and

reported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Nanoparticles (this work)	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (reported) <sup>5,6</sup>		
24.13	24.138		
33.16	33.158		
35.62	35.162		
39.31	39.27		
40.84	40.855		
43.51	43.515		
49.45	49.48		
54.19	54.091		
57.58	57.590		
62.44	62.451		
64.00	63.991		

#### References

- 1. C. G. Hardy, L. Ren, T. C. Tamboue and C. Tang, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1409-1420.
- 2. C. Tang, E. M. Lennon, G. H. Fredrickson, E. J. Kramer and C. J. Hawker, *Science*, 2008, **322**, 429-432.
- 3. C. Tang, J. Bang, G. E. Stein, G. H. Fredrickson, C. J. Hawker, E. J. Kramer, M. Sprung and J. Wang, *Macromolecules*, 2008, **41**, 4328-4339.
- 4. C. Tang, S.-m. Hur, B. C. Stahl, K.Sivanandan, M.Dimitriou, E. Pressly, G. H. Fredrickson, E. J. Kramer, C. J. Hawker, *Macromolecules*, 2010, **43**, 2880-2889.
- 5. B. K. Kuila, M. S. Rama and M. Stamm, *Adv. Mater.*, 2011, 23, 1797-1800.
- 6. S. Zhang, W. Wu, X. Xiao, J. Zhou, F. Ren and C. Jiang, *Nanoscale Res. Lett.*, 2011, **6**, 89.