



# Waterborne redox-active helix–coil–helix triblock metallopolymers: Synthesis, disassembly and electrochemical behaviors



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## ABSTRACT

Metallopolymers are emerging as a class of promising materials due to versatile properties and functionalities with a broad range of applications in high-performance devices. In this paper, a series of new helix–coil–helix poly( $\gamma$ -benzyl-L-glutamate)-*b*-poly(ethylene glycol)-*b*-poly( $\gamma$ -benzyl-L-glutamate) triblock copolymers selectively decorated with cyanoferrate complex (BEB-Fe) was successfully synthesized by combining ring-opening polymerization of  $\gamma$ -benzyl-L-glutamate carboxyanhydride using a primary amine terminated poly(ethylene glycol) as macromolecular initiator with a post-functionalization procedure. The polymers were characterized using GPC, NMR, UV–vis, FT-IR, CD, XRD, DLS, TEM, DSC and CV. Microstructural and morphological analysis revealed that incorporation of a proper amount of ferrate complex ( $\geq 19$  wt%) in BEB led to disassembly of hexagonally packed structures of EBE. This afforded hybrid nanostructures with a size of approximately 18 nm. Glass transition temperature of BEB-Fe increased gradually with increasing ferrate fractions. BEB-Fe hybrid nanomaterials were electrochemically active. The apparent diffusion coefficient of BEB-Fe was increased with increasing ferrate fractions.

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## 1. Introduction

Metallopolymers (or metal-containing polymers) are emerging as a class of promising materials due to versatile properties and functionalities. Metallopolymers combine the advantages of polymers including excellent flexibility and solubility with those of metal centers such as superior electrical conductivity, redox and catalytic properties [1–3]. Metallopolymers self assemble into nanomaterials with metal-enriched microdomains in bulk or solution, which offers a variety of applications in nano-devices [4–9].

Self-assembly of metallopolymers is driven by phase separation among the components. Self-assembly and resulting nanomaterials of metallopolymers is strongly dependent on their composition. To date a number of exquisite nanomaterials with varied morphologies including cylinder, sphere, nano-shell, nano-box, flowers have been achieved. PFS based copolymers (PFS: poly( $\pi$ -ferrocenyldimethylsilane)) self assembled into cylindrical micelles with PFS forming cores surrounded by a corona of the other blocks,

which is induced by crystallization of PFS block. The cylinders act as seeds and are capable of growing in a living manner when more copolymers were added [10–13]. Polyethylene terminated with cyanoferrate complex (PE-Fe) formed tiny flowers with ultrathin petals when crystallizing in xylene. The petals of flowers consisted of polyethylene lamellae sandwiched between two cyanoferrate complex nanolayers. The formation of the tiny flowers is a result of the interplay between polyethylene and ferrate complex [14]. For metal-decorated block copolymers synthesized by post-modification of copolymers with metal species, self-assembly is mainly dominated by parent block copolymers. Self-assembly of block copolymers induces metal species to aggregate regularly, affording nanomaterials with metal-enriched microdomains [15–21].

Nanomaterials produced through self assembly of metallopolymers have size in the range of 40 nm to hundreds of nanometers, depending on molecular weight of polymers. Metallopolymers with high molecular weight form large particles. While self-assembly of polymers with low molecular weight does not inevitably give rise to well-shaped tiny architectures due to decreased phase separation [20–23]. In particular, synthesis of polymer nanomaterials with small size ( $\leq 20$  nm) has been rarely reported likely due to the lack of proper polymers [24–26]. On the

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other hand, small nanoparticles exhibit enhanced performances due to large surface area and quantum effects, as demonstrated by experimental and theoretic results [27,28]. Synthesis of nanoparticles with small size is desirable for developing new materials with high performance, and is also crucial for fundamentally understanding the correlation between morphology and properties of nanomaterials.

Polypeptides show secondary structures induced by intramolecular and intermolecular hydrogen bonding in bulk or solution. Disassembly of such secondary structures appeared as a promising methodology for synthesis of tiny nanoparticles ( $\leq 20$  nm). Previously, we found that the incorporation of metal complex into 4-armed star poly( $\gamma$ -benzyl-L-glutamate) induced disassembly of secondary structures, affording a catalog of anisotropic hybrid nanoparticles [24–26]. Encouraged by this finding, in this study we synthesized linear helix–coil–helix poly( $\gamma$ -benzyl-L-glutamate)-*b*-poly(ethylene glycol)-*b*-poly( $\gamma$ -benzyl-L-glutamate) triblock copolymers selectively decorated with cyanoferrate complex (BEB-Fe). Microstructural and morphological analysis revealed that incorporation of a proper amount of ferrate complex ( $\geq 19$  wt%) in BEB led to disassembly of hexagonally packed structures of poly( $\gamma$ -benzyl-L-glutamate), giving rise to hybrid nanostructures with a size of approximately 18 nm that is inaccessible to conventional amphiphilic block copolymers [29–34]. Although poly( $\gamma$ -benzyl-L-glutamate) (PBLG) based block copolymers have been intensively investigated, disassembly behaviors of such PBLG based copolymers have been rarely reported to our best knowledge. BEB-Fe hybrid nanomaterials were electrochemically active. Such metal-containing block copolymers offer an unique opportunity for the synthesis of functional tiny nanostructures.

## 2. Experimental section

### 2.1. Characterization

Molecular weight and molecular weight distribution of BEB and BEB-Fe synthesized were determined using gel permeation chromatography (GPC) (Waters Breeze 2417) calibrated with PEO standard and with DMF as eluent.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of BEB and BEB-Fe were carried out using Mercury-Plus 300 (VARIAN). To improve the solubility of BEB in  $\text{CDCl}_3$ , ca. 15 vol% trifluoroacetic acid (TFA) was added for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR measurement. X-ray Diffraction (XRD) measurements were performed using XRD diffractometer (D-MAX 2200 VPC) equipped with Ni-filtered  $\text{Cu K}\alpha$  radiation, having a wavelength of 0.154 nm. The diffractometer was scanned in  $2\theta$  range from  $1.5^\circ$  to  $50^\circ$  and the scanning rate used was  $1.2^\circ\text{min}^{-1}$ . UV–vis spectroscopy data were obtained by use of a Hitachi U3500 at room temperature. FT-IR spectra were recorded using a Nicolet/Nexus 670 FT-IR spectrophotometer. Powder samples were mixed with KBr and then pressed into pellets for FT-IR measurements. Circular dichroism (CD) measurements were recorded on a Jasco J-720 spectropolarimeter in 1 mm quartz cuvettes with a step resolution of 0.2 nm, a scan speed of 50 nm/min, a sensitivity of  $0.1^\circ$ , and a response time of 9.5 s. Each spectrum was the average of 5–10 scans. Dynamic light scattering (DLS) measurement was performed using a Brookhaven instrument. Scattering angle was fixed at  $90^\circ$ . A field emission gun TEM microscope (JEM2010HR) equipped with an Oxford instrument UTW ISIS EDX system was used to characterize the microstructure of BEB-Fe. Acceleration voltage was 200 kV. BEB-Fe was dispersed in distilled water with the assistance of sonication (0.05 mg/mL). The sample was prepared by adding a drop of BEB-Fe/water suspension on a carbon-coated copper grid. The sample was firstly frozen with liquid  $\text{N}_2$  and sublimation under reduced pressure. The specimen was directly observed without

staining due to the presence of iron elements. DSC measurement was carried out using a Perkin–Elmer DSC-7 instrument under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The temperature was calibrated with indium prior to the test. Cyclic voltammetry was performed by using a CHI-660D electrochemical analyzer (CH instruments, Inc.) in a three electrode cell. Glassy carbon working electrodes with a diameter of 3 mm were polished with slurry of  $0.05\ \mu\text{m}$  alumina particles, sonicated and rinsed with ultrapure water. After drying under  $\text{N}_2$  flow, the glassy carbon working electrodes were made hydrophilic by the treatment in oxygen plasma (1 Torr  $\text{O}_2$ , 10 W) for 5 min. The cleaning process was repeated until no voltammetric features were observed between  $-0.2$  and  $0.8$  V (vs  $\text{Ag}/\text{AgCl}$ ) at the scan rate of  $100\ \text{mV}/\text{s}$  in  $0.1\ \text{M}$  KCl solution. BEB-Fe dispersed in ultrapure water was deposited on freshly cleaned glassy carbon working electrodes. The solvent was allowed to evaporate at room temperature overnight. To remove oxygen, the KCl solution was degassed by bubbling  $\text{N}_2$  for 40 min prior to CV measurements. Each sample was tested three times to obtain reproducible results.

### 2.2. Synthesis

#### 2.2.1. Synthesis of poly( $\gamma$ -benzyl-L-glutamate)-*b*-poly(ethylene glycol)-*b*-poly( $\gamma$ -benzyl-L-glutamate) triblock copolymer (BEB, **2**)

0.11 g macromolecular initiator **1** (0.05 mmol) (see Supporting Information, Scheme S1) and 2.8 g  $\gamma$ -benzyl-L-glutamate carboxyanhydride (BLG-NCA) (11 mmol) were dissolved in 50 mL anhydrous THF and the solution was stirred for 72 h at room temperature under  $\text{N}_2$ . The resulting mixture was added dropwise to ethanol. The precipitate was isolated by filtration and dried under vacuum at  $40^\circ\text{C}$  overnight to yield poly( $\gamma$ -benzyl-L-glutamate)-*b*-poly(ethylene glycol)-*b*-poly( $\gamma$ -benzyl-L-glutamate) triblock copolymer (BEB, **2**) as white solids.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3+15\text{vol}\%$  TFA, 298 K):  $\delta$  1.90–2.24 (br, 424H,  $\text{COCH}_2\text{CH}_2$ ), 2.41–2.69 (br, 424H,  $\text{COCH}_2\text{CH}_2$ ), 3.65 (br, 180H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 4.58 (br, 212H,  $\text{COCHNH}$ ), 5.12 (m, 424H,  $\text{COOCH}_2\text{Ph}$ ), 7.28–7.42 (br, 1060H,  $\text{COOCH}_2\text{Ph}$ ), 7.92 (br, 212H,  $\text{CONH}$ ).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3+15\text{vol}\%$  TFA, 298 K):  $\delta$  26.3 and 29.4 ( $\text{CH}_2$ ), 52.7 ( $\text{NHCHCO}$ ), 67.6 ( $\text{CH}_2\text{Ph}$ ), 68.8 ( $\text{OCH}_2\text{CH}_2\text{O}$ ), 127.7 and 133.3 ( $\text{Ph}$ ), 172.4 and 174.6 ( $\text{C=O}$ ). FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1655 (C=O stretching of  $\alpha$ -helix), 1545 (C–N stretching of  $\alpha$ -helix).

#### 2.2.2. Synthesis of ferrate-containing BEB (BEB-Fe)

Prescribed amount of BEB in 20 mL DMF was mixed with  $\text{NH}_4\text{Na}_2[\text{Fe}(\text{II})(\text{CN})_5\text{Py}]$  in 10 mL methanol. The mixture was stirred at  $40^\circ\text{C}$  for 72 h in dark under  $\text{N}_2$ . The product was precipitated by adding the reaction mixture dropwise to 100 mL cold methanol with vigorously stirring, centrifuging and decanting the top-layer solution. The solid was purified by repeatedly dissolving in 10 mL DMF, precipitating from 100 mL methanol, centrifuging until top-layer solution is clear and colorless. The solid was dried in vacuum at  $40^\circ\text{C}$  overnight to yield ferrate-containing BEB (BEB-Fe). BEB-Fe26:  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , 298 K):  $\delta$  1.90–2.24 (br, 424H,  $\text{COCH}_2\text{CH}_2$ ), 2.41–2.69 (br, 424H,  $\text{COCH}_2\text{CH}_2$ ), 3.50 (br, 180H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.88–4.20 (br, 92H,  $\text{COCHNH}$ ), 4.98 (br, 209H,  $\text{COOCH}_2\text{Ph}$ ), 7.22 (br, 543H,  $\text{COOCH}_2\text{Ph}$ ), 8.15 (br, 86H,  $\text{CONH}$ ). Integrate of the resonance peaks of BEB-Fe were not consistent with those of BEB possibly due to decreased solubility induced by incorporation of cyanoferrate complex.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ , 298 K):  $\delta$  3.57 (s, 2H,  $\text{OCH}_2\text{CH}_2\text{O}$  from PEG segments), 7.32 (d, 2H, Py from ferrate complex), 8.88–8.98 (d, 2H, Py from ferrate complex). All BEB-Fe synthesized showed similar FT-IR spectra. FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 2060 (C $\equiv$ N stretching), 1735 (C=O stretching), 1653 (C=O

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