

Synthesis and Solution Self-Assembly of Side-Chain Cobaltocenium-Containing Block Copolymers

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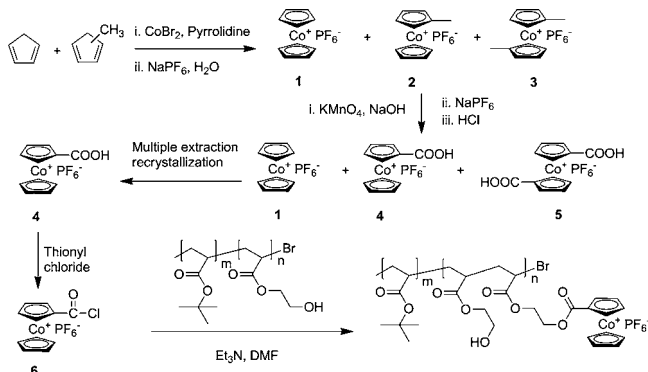
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Among metallocopolymers,¹ metallocene-containing polymers have attracted significant attention since they have great potential in catalytic, optical, magnetic, and biological applications due to the unique geometries and physicochemical properties of metallocenes.² Compared to widely studied ferrocene and ferrocene polymers,^{1,2} cobaltocene has received far less attention, partly because of the greater difficulty in preparing substituted derivatives.³ Cobaltocene (19-e) has one more valence electron than ferrocene (18-e). The ionization potential of cobaltocene is 5.56 eV,⁴ only slightly above that of alkali metals, so cobaltocene can lose an electron readily to form the cobaltocenium cation (18-e),⁵ isoelectronic with ferrocene. Given the ease oxidation of cobaltocene and the great inertness of cobaltocenium salts, it is extremely difficult to prepare substituted derivatives from cobaltocene or cobaltocenium. Although a few main-chain cobaltocenium polymers were synthesized via condensation or ring-opening polymerization,⁶ there have been almost no reports on the synthesis of side-chain cobaltocenium polymers.⁷ Due to their cationic nature, side-chain cobaltocenium polymers exhibit interesting solubility behaviors. For example, we found that cobaltocenium acrylate polymers with PF₆⁻ as anions are soluble in water and acetone but not soluble in less polar solvents such as chloroform. Thus, the cationic features and unique solubility of cobaltocenium-containing block copolymers may present interesting solution self-assembly, which could lead to useful catalytic, magnetic, and redox properties.

As the first step toward developing this class of organometallic polymers, herein we report novel side-chain cobaltocenium-containing block copolymers and their solution self-assembly, starting with unambiguous evidence on the synthesis of highly pure monocarboxycobaltocenium. As shown in Scheme 1, our synthetic strategy is based on the preparation of a block copolymer substrate followed by attachment of cobaltocenium to one of the blocks. Synthesis of pure (~100%) monocarboxycobaltocenium is a vital step toward side-chain cobaltocenium polymers, as trace amounts of coexisting 1,1'-disubstituted cobaltocenium could result in cross-linked polymers. We modified a procedure reported by Sheats and co-workers^{3a} with exhaustive extraction and recrystallization to remove any remaining 1,1'-dicarboxycobaltocenium. Nearly 100% pure monocarboxycobaltocenium **4** with an overall yield of 14–20% was obtained. The structures and purity of compound **4** were confirmed by ¹H and ¹³C NMR and MS spectra (Figures S1–S5, Supporting Information (SI)), with three different characteristic chemical shifts of cyclopentadienyl (Cp) protons in the ¹H NMR spectrum (Figure S3), while ¹H NMR of dicarboxycobaltocenium **5** showed a different and characteristic A2B2 pattern of Cp protons (two peaks, unresolved; Figure S3). The monocarboxycobaltocenium **4** was readily converted into the relatively stable cobaltocenium acyl chloride **6** under reflux of thionyl chloride.

The cobaltocenium moiety was then attached to side chains of block copolymers through reaction between the acyl chloride **6** and

Scheme 1. Synthesis of Monocarboxycobaltocenium and Side-Chain Cobaltocenium-Containing Block Copolymers



poly(*tert*-butyl acrylate)-*block*-poly(2-hydroxyethyl acrylate) (PBA-*b*-PHEA-Br). Well-defined block copolymers PBA-*b*-PHEA-Br with polydispersity indexes < 1.2 were prepared by atom-transfer radical polymerization (ATRP). A bromine-terminated poly(*tert*-butyl acrylate) (PBA-Br) macroinitiator was synthesized and then chain-extended with 2-hydroxyethyl acrylate. With the same starting PBA-Br, different block lengths of PHEA or relative ratios of PHEA and PBA-Br were achieved by controlling the conversion of HEA monomers during polymerization. In this study, we focus on one well-defined block copolymer, PBA₈₀-*b*-PHEA₃₈. The esterification reaction of PBA-*b*-PHEA-Br with cobaltocenium acyl chloride **6** was performed with the aid of triethylamine in dimethylformamide. Figure 1 shows the ¹H NMR spectra of PBA-*b*-PHEA-Br and resulting PBA-*b*-poly(2-acryloyloxyethyl cobaltoceniumcarboxylate) (PBA-*b*-PAECo-Br). Chemical shifts at 3.6 and 4.2 ppm corresponded to the ethyl protons of PBA-*b*-PHEA-Br.

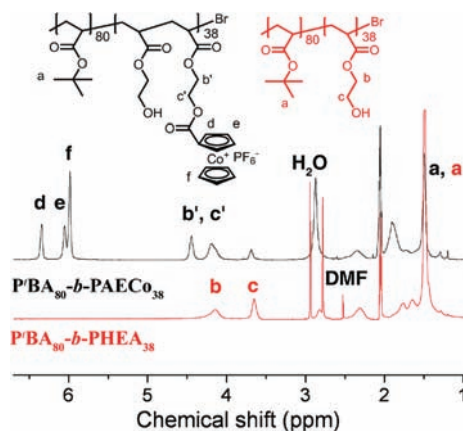


Figure 1. ¹H NMR spectra of PBA-*b*-PHEA-Br and PBA-*b*-PAECo-Br block copolymers in acetone-*d*₆.

After esterification, characteristic chemical shifts at 5.8–6.4 ppm corresponded to protons from Cp of the cobaltocenium units. Moreover, ethyl protons from cobaltocenium-linked units shifted to lower field around 4.4 ppm, indicating the successful attachment of cobaltocenium to the side chains of block copolymers. However, due to possible steric hindrance of bulky cobaltocenium units, the esterification yield was about 70%, as a small peak at 3.6 ppm was observed in the P'BA-*b*-PAECo-Br block copolymers, corresponding to ethyl protons from unreacted PHEA block. Thermogravimetric analysis (Figure S10, SI) indicated that these block copolymers have three stages of weight loss: 200–280, 300–500, and 850 °C and above, respectively corresponding to decomposition of *tert*-butyl group, complete degradation of polymer skeleton derived from P'BA-*b*-PHEA-Br precursors, and decomposition of Cp rings from cobaltocenium. A plateau between 500 and 850 °C was observed and assigned to cobaltocenium salts, indicating high thermal stability of cobaltocenium structures.

We then explored self-assembly behaviors of cobaltocenium-containing block copolymers in solution. The micellization of P'BA-*b*-PAECo-Br was first carried out by dissolving the block copolymers in acetone and then adding water to induce micelle formation. PAECo blocks are soluble in both acetone and water, while P'BA is soluble only in acetone. Figure 2a shows the P'BA-*b*-PAECo-Br block copolymer micellar aggregates in acetone and water mixture. Transmission electron microscopy (TEM) images show that these micellar aggregates exhibited vesicle morphology. These vesicles are not uniform, with diameter ranging from 50 to 300 nm. In unstained TEM images, we were only able to see the electron-rich cobaltocenium-containing PAECo domains. Thus, we believe that the dark rings are formed by the PAECo blocks. Size analyses from dynamic light scattering (DLS) experiments (Figure 2b) indicated that the hydrodynamic radius of vesicles falls into two major populations, 50 ± 30 and 240 ± 120 nm, consistent with TEM results.

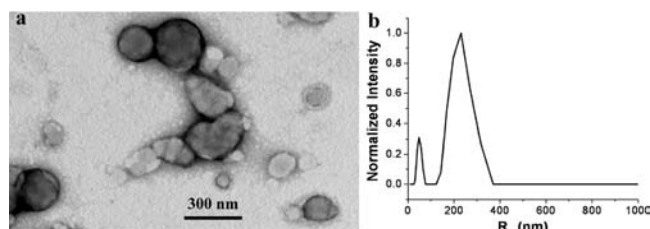


Figure 2. (a) Bright-field TEM micrograph and (b) size distribution (from DLS) of P'BA-*b*-PAECo-Br micellar aggregates in acetone and water mixture.

We also examined the micellar morphology in chloroform by adding this solvent to the solution of P'BA-*b*-PAECo-Br block copolymers in acetone. PAECo block is not soluble in chloroform. Representative TEM micrographs (Figures 3 and S12–S14, SI) show that self-assembled micelles have straight nanotubular structures in the mixture of acetone and chloroform. Although the length of nanotubes ranges from 1 to 4 μm , the nanotubes have quite uniform diameter, ca. 50 ± 5 nm, with an average of wall thickness of 12 ± 2 nm and an average cavity width of 26 ± 3 nm. Figure 3a clearly demonstrates that the nanotubes have darker walls, corresponding to electron-rich PAECo domains, with the center much lighter than the walls.

Additional evidence of such nanotubular structures were further obtained by performing TEM under dark-field mode.⁸ As shown in Figure 3b, the center of the nanotubes is darker than the shell,

indicating that the center is the cavity of the nanotubes while the shell contains electron-rich PAECo domains. Direct comparison of the same areas of samples between bright-field and dark-field modes further indicated the formation of nanotubular structures (Figure S14).

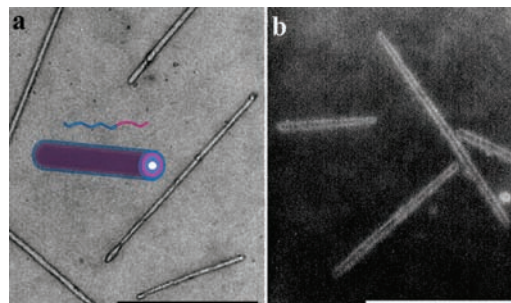


Figure 3. TEM micrographs of P'BA-*b*-PAECo-Br self-assembled aggregates in the mixture of acetone and chloroform. Samples were viewed (a) under bright-field mode and (b) under dark-field mode. The inset in panel a is a proposed illustration of the self-assembled nanotubes. Scale bar: 1000 nm.

In conclusion, we have synthesized highly pure monosubstituted carboxycobaltocenium and subsequently prepared side-chain cobaltocenium-containing block copolymers. These block copolymers exhibited self-assembled vesicle and nanotube structures depending on the solvent system used. Currently, effects of different anions and hydrophobic blocks on the micellar morphology are under investigation.

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Supporting Information Available: Experimental details and complete characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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