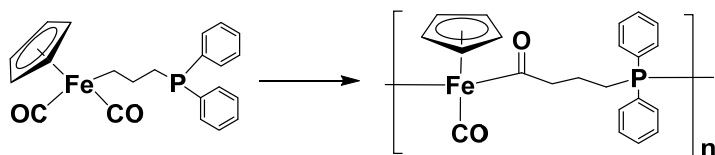


# Synthesis and Self-Assembly of Main-Chain Metal Carbonyl Organometallic Macromolecules Prepared by Migration Insertion Polymerization

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## 1. Introduction

Metal carbonyl organometallic macromolecules have attracted considerable attention due to its applications in CO delivery, electron beam lithography and magnetic materials. However, synthesis of this group of polymers is a challenge because of the instability of metal carbonyl monomers and the corresponding polymers. It is therefore desirable to create new polymerization technique. Migration insertion polymerization (MIP) is a newly developed polymerization technique, in which a bifunctional molecule  $[\eta^5\text{-C}_5\text{H}_5]\text{Fe}(\text{CO})_2(\text{CH}_2)_3\text{PPh}_2$  (FpP) is used as a monomer.<sup>1-3</sup> The resulting polymers, PFpPs, are stable in air and soluble in common organic solvents. End group analysis indicates that the polymer has a linear chain with Fp and phosphine end groups. End group functionalization has been performed via a migration insertion reaction in the presence of alkyl phosphine derivatives.<sup>4</sup> In addition, It has been discovered that the homopolymer PFpP is able to self-assemble into uniform and stable vesicles in water.<sup>5</sup>



**Scheme 1.** Migration insertion polymerization of FpP.

## 2. Experiment

### 2.1 Polymerization of FpP

MIP of FpP was carried out in bulk at an elevated temperature. After a desired reaction time, the polymerization was terminated by cooling the reaction flask to 23 °C. Afterwards, the crude product was dissolved using a small amount of THF, then the solution was precipitated into a large amount of hexane, the yellow precipitates were collected by filtration and dried under vacuum overnight.

## 2.2 End group functionalization

PFpP with  $DP_n = 7$  (700.0 mg, 0.25 mmol) and excess amounts of alkyldiphenylphosphines were dissolved in 30.0 mL THF. The reaction mixture was then refluxed at 70 °C under N<sub>2</sub> atmosphere. After a desired reaction time, the reaction mixture was cooled to 25 °C and the solutions were subsequently concentrated under vacuum. The concentrated solution was precipitated in a large amount of hexane and the precipitate was collected *via* filtration. For the reaction system with Ph<sub>2</sub>PC18, the precipitate was further washed with 2.0 mL methanol three times in order to remove the remaining Ph<sub>2</sub>PC18. The yellow precipitate was dried under vacuum at 25 °C.

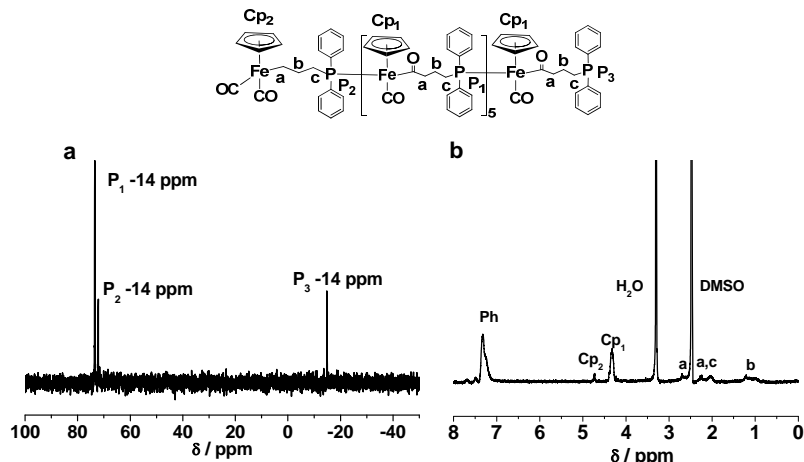
## 2.3 Preparation of PFpP colloidal solution

Different amounts of PFpPs were dissolved in 1.00 mL THF, yielding clear yellow solutions. The solutions were then filtered through PTFE membranes with a pore size of 0.22 μm. To these THF solutions, 10.00 mL of deionized water was injected. THF was subsequently removed via N<sub>2</sub> bubbling for 1 h.

## 3. Results and Discussion

### 3.1 Synthesis and characterization of PFpP

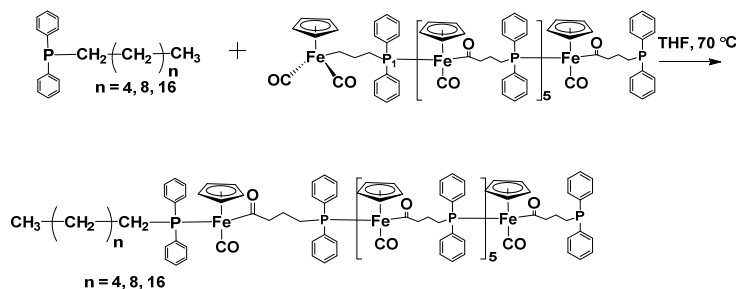
PFpP was synthesized by heating FpP in bulk at an elevated temperature. At 70 °C, PFpP oligomers with  $DP_n = 7$  were produced. The resulting products were also characterized by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopies. As shown in Figure 1a, three peaks at 73 ppm (P<sub>1</sub>), 72 ppm (P<sub>2</sub>) and -14 ppm (P<sub>3</sub>) are observed in the <sup>31</sup>P NMR spectrum, which can be assigned to the main chain coordinated phosphorus (P<sub>1</sub>), the chain end coordinated phosphorus (P<sub>2</sub>) and the uncoordinated phosphine end group (P<sub>3</sub>), respectively. The <sup>1</sup>H NMR spectrum for PFpP was displayed in Figure 1b, the resonance signals at 4.7 ppm and 4.3 ppm represent the Cp ring in the chain end group (Cp<sub>2</sub> in Figure 1b) and the Cp rings in the Fp acyl repeat units (Cp<sub>1</sub> in Figure 1b), respectively. The presence of the unreacted Fp group indicates that the PFpP oligomer can be further functionalized via a migration insertion reaction in the presence of phosphine ligands. When the polymerization was performed at 105 °C in the presence of 5 wt% DMSO, relatively high molecular weight PFpP with M<sub>n</sub> up to 25,700 g/mol was obtained.



**Figure 1.** (a)  $^{31}\text{P}$  and (b)  $^1\text{H}$  NMR spectra for PFpP produced from bulk polymerization of FpP at  $70\text{ }^\circ\text{C}$ .

### 3.2 End group functionalization

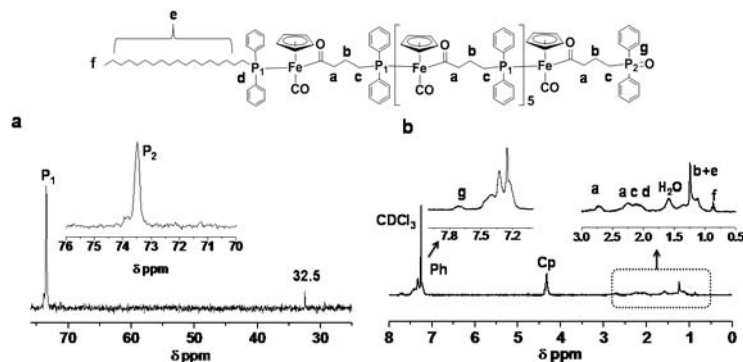
Taking advantage of the reactivity of the Fp end group in PFpP oligomers, a series of alkyldiphenylphosphine functionalized PFpP were prepared via migration insertion reaction of the Fp end groups in the presence of  $\text{Ph}_2\text{PCn}$  ( $n = 6, 10, 18$ ) (Scheme 2).



**Scheme 2.** Preparation of alkyldiphenylphosphine functionalized PFpP amphiphiles.

The resulting products were characterized using  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopies. As illustrated in Figure 2a, the  $^{31}\text{P}$  NMR spectrum shows two peaks at 73.5 ppm ( $\text{P}_1$  in Figure 2a) and at 32.5 ppm ( $\text{P}_2$  in Figure 2a), which can be assigned to the coordinated phosphorus and the oxidized phosphine end group, respectively. The  $^1\text{H}$  NMR spectrum of the molecules (Figure 2b) shows that the signal at 4.5 ppm, due to the Cp ring for the

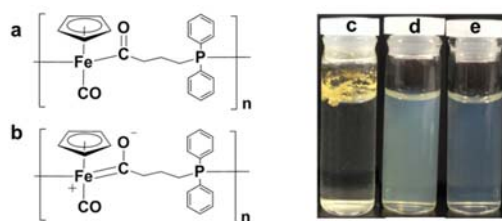
Fp end group, upfield shifted as a result of MIR and merged with the rest of Cp rings in the main chain (4.3 ppm).



**Figure 2.** (a)  $^{31}\text{P}$  NMR and (b)  $^1\text{H}$  NMR spectra for  $\text{Ph}_2\text{PC18}$  functionalized PFpP amphiphiles in  $\text{CDCl}_3$ .

### 3.3 Self-assembly of PFpP in water

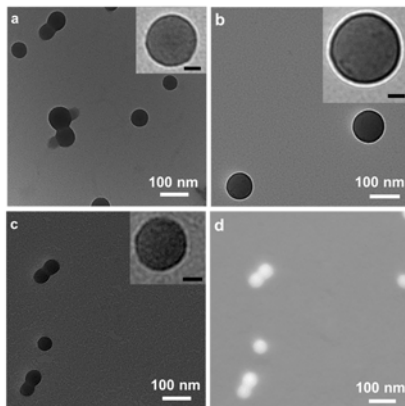
When we quickly inject water into a THF solution of PFpPs followed by  $\text{N}_2$  bubbling to remove THF, the polymer is uniformly dispersed in the solution. Figures 3d and e illustrate the aqueous solutions of PFpPs with varied concentrations. Both solutions show a blue tint, suggesting that colloids are formed.



**Figure 3.** (a) Chemical structure of PFpP; (b) PFpP resonance structure; (c) Hydrophobic PFpP floating on water; (d) PFpP colloids in water (0.1 mg/mL) and (e) (0.05 mg/mL). Note: The degree of polymerization for PFpP is 20.

The morphology of the PFpP colloids was characterized by TEM. When the TEM with a high voltage electron beam (60 kV or 200 kV) is used, particles with a relatively darker periphery are observed, suggesting that the spherical nanoparticles are vesicles (Figure 4a, b and c). TEM was also performed in the dark-field mode. As shown in Figure 4c, the

vesicles are bright due to strong electron scattering resulting from the irons in PFpPs. The vesicle structure has also been confirmed by a combination of DLS and SLS measurements.



**Figure 4.** TEM images for PFpP vesicles obtained from (a, b) 60 kV TEM; (c) 200 kV TEM; (d) 200 kV TEM in bright-field mode. The scale bar for the insets in a, b and c is 20 nm.

#### 4. Conclusion

Migration insertion polymerization has been developed, which generates air stable and soluble main-chain metal carbonyl organometallic macromolecules. The end group of the polymers can be further functionalized. The resulting iron carbonyl homopolymer PFpP can self-assembly into uniform vesicles in water.

#### 5. References

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