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# Migration Insertion Polymerization (MIP) of Cyclopentadienyldicarbonyldiphenylphosphinopropyliron (FpP): A New Concept for Main Chain Metal-Containing Polymers (MCPs)

Xiaosong Wang,* Kai Cao,† Yibo Liu,† Brian Tsang, and Sean Liew

Department of Chemistry and Waterloo Institute of Nanotechnology, University of Waterloo, 200 University Avenue, Waterloo, Canada N2L 3G1

*Supporting Information*

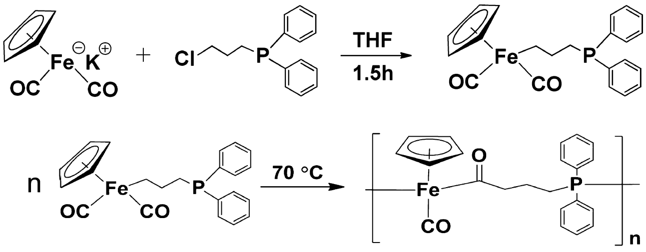
**ABSTRACT:** We report a conceptually new polymerization technique termed migration insertion polymerization (MIP) for main chain metal-containing polymer (MCP) synthesis. Cyclopentadienyldicarbonyldiphenylphosphinopropyliron (FpP) is synthesized and polymerized via MIP, resulting in air stable poly(cyclopentadienylcarbonyldiphenylphosphinobutanoyliron) (PFpP) displaying narrow molecular weight distribution. The backbone of PFpP contains asymmetric iron units connected by both phosphine coordination and Fe-acyl bonds, which is representative of a new type of polymer. Furthermore, PFpP is tested to be soluble in a wide range of organic solvents and shown to possess reactive Fp end groups. PFpP amphiphiles have therefore been prepared via an end group migration insertion reaction in the presence of oligoethylene phosphine.

The development of synthetic chemistry for metal-containing polymers (MCPs)[1] has led to exciting progress in living supramolecular chemistry[2] and in applications for modern technologies,[3] e.g. solar cells,[4] security ink,[5] and self-healing smart materials.[6] To date, most organometallic monomers are polymerized using well-developed techniques such as ring-opening polymerization,[7] condensation,[8] and living chain polymerization.[9] During the polymerization, metal coordination structures usually remain intact. Either organic or inorganic[10] reactive groups pending from metal ligands are actually responsible for the growth of polymer chains. Organometallic propagating reactions for macromolecule synthesis are rarely explored but offer opportunities for innovative chemistry and for creation of novel polymers. For example, by taking advantage of the photolability of metal coordination bonds, ring-opening photopolymerization can be carried out under mild conditions.[11,12] Soluble metal coordination chain polymers have been made using "complex as metal" strategies,[13] or direct metal coordination chemistry.[14] Metal carbon $\sigma$-bonds have been built into transition metal acetylide polymer backbones using oxidative coupling reactions.[1,4]

For organometallic compounds containing cisoidal anionic and neutral ligands, migration insertion reactions (MIRs) often occur to combine two ligands into a new anionic ligand. After MIR, there is no change in the oxidation state of the metal center, but the overall electron count of the metal decreases by 2e$^-$. As a result, this allows a neutral ligand to coordinate via the empty orbital.[19] We therefore envision that MIRs[15] can be used to link organometallic units together into a macromolecular chain structure through rational design of organometallic monomers. For example, A−B type monomers can be designed with organometallic groups capable of MIR acting as (A) and neutral phosphine ligands acting as (B). To explore the possibility of this new polymerization concept, cyclopentadienylironcarbonyl (Fp) chemistry[15] is used for the synthesis of monomers and MCPs.[7c,16] It is well-known that the reaction of alkyldicarbonylcyclopentadienyliron (FpR) with nucleophilic ligands, e.g. phosphine ($PR_3$), leads to air stable phosphine coordinated acyl complexes as a result of MIR.[17] We therefore expect that molecules containing both Fp and phosphine groups can act as a difunctional A−B type monomer used for macromolecule construction via a migration insertion polymerization (MIP) process.

In this communication, we report a proof-of-concept that MIP occurred as designed through bulk polymerization of the monomer, cyclopentadienyldicarbonyldiphenylphosphinopropyliron (FpP) (Scheme 1). The resulting polymer, poly(cyclopentadienylcarbonyldiphenylphosphinobutanoyliron) (PFpP), contains asymmetric iron units connected by phosphine coordination and metal−acyl bonds representing a new type of MCP. The polymer exhibits narrow molecular weight distribution and is soluble in many organic solvents: THF, DCM, DMF, etc. The Fp end groups of FpP remain reactive and can be used for end group functionalization via an MIR coupling reaction.

**Scheme 1. Scheme for Synthesis and MIP of FpP**



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The monomer (FpP) was prepared from a salt-elimination reaction between 1-chlorodiphenylphosphinopropane and potassium cyclopentadienyldicarbonyliron (FpK) at room temperature. The IR spectrum of the resulting compound reveals two absorption frequencies for CO at 1952 and 2004 cm$^{-1}$ (Figure S1). This suggests that only terminal CO exists as designed.[24] In addition, the existence of phosphine groups is confirmed by $^{31}$P NMR (Figure 1). $^{1}$H NMR analysis reveals a peak at 1.46 ppm representing protons for $-CH_2-$Fe (Figures 1, S2, and S3).[19] This suggests that the carbon−iron bond is produced from the substitution reaction between the chloride and the Fp metalate. The integration ratio between the Cp (4.8 ppm) and phenyl protons (7.28−7.40 ppm) is 1:2. This indicates that the monomer possesses equal amounts of Fp and phosphine groups as designed. However, FpP undergoes intramolecular cyclic reactions in diluted organic solvents (see Supporting Information).[20]

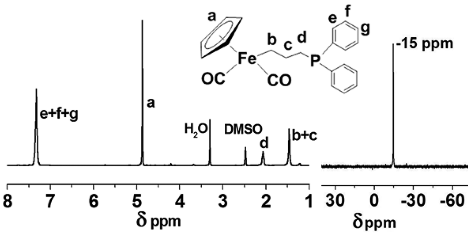

**Figure 1.** $^{1}$H and $^{31}$P NMR spectra of FpP in DMSO-$d_6$.

Since MIR can also occur in solid state,[18,21] bulk polymerization of FpP was performed at 70 °C to suppress intramolecular cyclic reactions. During the polymerization, the viscosity of the system gradually increased until glass-like solid material was produced with the stir bar frozen inside the product. To terminate the polymerization, the reaction flask was first cooled to room temperature. Then THF was added to dissolve the solid products. Afterward, the clear solution was transferred dropwise into hexane obtaining pale yellow precipitates. For the sample that polymerized longer than 18 h, the precipitates were recovered in an almost quantitative yield. Also the supernatant of the mixture was colorless indicating that most of the organometallic monomers participated in the polymerization. The resulting precipitates are readily soluble in many solvents such as THF, DMSO, DCM, acetone, DMF, toluene, benzene, and chloroform but are insoluble in water and nonpolar solvents such as hexane. All of the polymer solutions (yellow) were left exposed to air, which resulted in no obvious color change and precipitation during the experimental period of 4 days.

The macromolecular nature of the products was shown by GPC with either THF or DMF eluents. There were no changes in GPC traces for the same samples characterized immediately and 2 days later. This confirmed that the polymers are sufficiently stable in solution and can be used for further studies. GPC results for the polymers are summarized in Table 1. As shown in Table 1, by increasing the time, the molecular weight ($M_n$) gradually increased. This result suggests MIP occurs. Interestingly, all polymers exhibit narrow molecular weight distributions with polydispersities in the range between 1.09 and 1.33. These values are much narrower compared to the expected PDI (ca. 2) for polymers produced from a conventional step growth polymerization, in which the monomer functional groups and polymer end groups are assumed to have equal reactivity. The unexpected narrow PDI for the polymers produced from MIP can be rationalized by the low reactivity of the phosphine end group of PFpP (Figure S4). It has been reported that phosphine with bulk groups slow down MIRs.[17,22] In the case of polymerization, increased steric effects are expected from the formation of macromolecular chains. Therefore, small molecules are expected to react faster than larger molecules leading to the observed narrow PDI. A detailed investigation of this phenomenon is currently underway.

**Table 1. GPC Results for PFpP Prepared from Migration Insertion Polymerization of FpP[a]**

| entry | time/h | yield[b] | $M_w$ | $M_n$ (GPC/NMR) | PDI | DP[d] |
|---|---|---|---|---|---|---|
| 1 | 5 | 69 | 3920 | 3320/3230 | 1.18 | 8 |
| 2 | 12 | 75 | 7240 | 6640/6460 | 1.09 | 16 |
| 3 | 16 | 85 | 13090 | 9870/9700 | 1.33 | 24 |
| 4 | 18 | >95 | 15500 | 12100/−[e] | 1.28[f] | 30 |

[a]Polymerization were performed in bulk at 70 °C. [b]Polymers were isolated by precipitation of THF solution in hexane. Yields are obtained by gravimetric analysis. [d]DP: degree of polymerization. [e]End group is invisible in NMR. [f]Sample for GPC was taken right after the polymerization without precipitation.

DSC analysis (Figure 2) indicates that PFpP has a $T_g$ of ca. 100 °C. This $T_g$ is well above room temperature and demonstrates a thermoplastic characteristic of the polymer. TGA analysis (Figure 2) indicates that the polymer loses ca. 60% of its original weight at 180 °C. The second stage of weight loss starts at 432 °C. Finally, the polymer loses ca. 77% of its original weight at 622 °C leaving ca. 23% char yield.

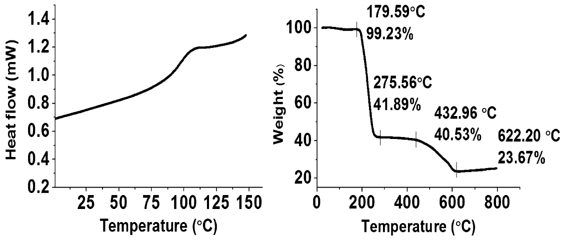

**Figure 2.** DSC and TGA curves for PFpP.

The molecular structure of PFpP was established by IR and NMR spectroscopies. The IR spectrum reveals two absorption frequencies at 1910 and 1600 cm$^{-1}$ (Figure S1). This indicates the presence of both terminal CO and inserted carbonyl groups in the polymers as a result of an MIR.[24] This is further verified by $^{13}$C NMR analysis which shows resonance peaks at 219 and 272 ppm (Figure S5) corresponding to terminal CO and acyl groups respectively.[24] The $^{31}$P NMR reveals a new signal appearing at 73 ppm that represents the coordination of phosphines to iron centers.[24]

The $^{1}$H NMR analysis (Figure 3) of PFpP also shows evidence of MIR. The Cp ring of PFpP at 4.3 ppm is shifted upfield compared to the Cp ring of FpP (Figure 3). This upfield shift provides evidence of phosphine assisted MIR occurring.[17] The small peak displayed at 4.7 ppm is assigned to the Cp ring of the Fp end group of PFpP. The peaks at 2.8 and 2.3 ppm are assigned to two diastereotopic protons from the C(O)$CH_2$ acyl groups adjacent to the Fe chiral center.[17] This assignment is confirmed by $^{13}$C−$^{1}$H HMQC 2D NMR (Figure S6). The signal at 2−2.2 ppm is assigned to the central $CH_2$ protons, and

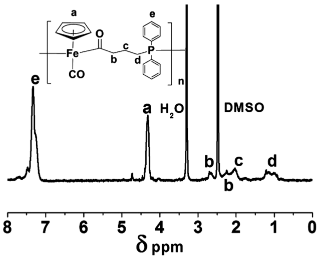

**Figure 3.** $^1$H NMR spectrum for PFpP ($M_n$ = 6640, $M_w/M_n$ = 1.09) in DMSO-$d_6$.

the signal at 0.9−1.3 ppm is assigned to the protons adjacent to $P(Ph)_2$.[24] These signals have an integration ratio of 1:1. The integration ratio of the phenyl protons at 7.1−7.8 ppm relative to the Cp ring at 4.3 ppm is 2:1, which is in agreement with the targeted molecular structure of PFpP.

Figure 4 shows $^{31}$P and $^1$H NMR spectra of the polymers with an $M_n$ of 3320 g/mol. Three peaks at 73, 72, and −14 ppm that appeared in $^{31}$P NMR can be assigned to the main chain coordinated phosphorus, chain end coordinated phosphorus, and uncoordinated phosphine end group, respectively. Their integration ratio of 6:1:1 suggests that the polymer has a degree of polymerization (DP) of 8. The DP estimated from GPC characterization of the polymers is also 8 (Table 1). These results suggest that the resulting polymers are linear chains without closed rings. The integration ratio between the resonances at 4.3 ppm labeled (a) in Figure 4 and at 4.7 ppm labeled (b) is 7:1. From the integration ratio and the fact that the DP is 8, the chemical shift at 4.7 ppm can be confirmed as the Cp ring of the Fp end group (Figure 4).

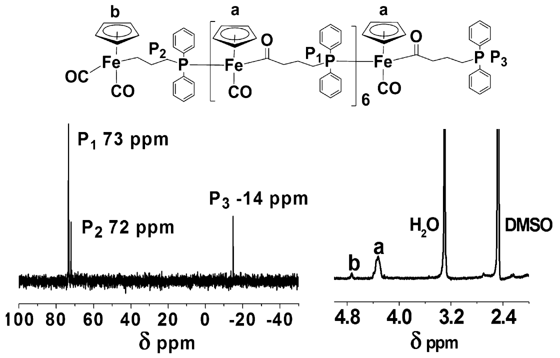

**Figure 4.** $^{31}$P and $^1$H NMR spectra of PFpP ($M_n$ = 3320, $M_w/M_n$ = 1.18) in DMSO-$d_6$.

Taking advantage of the reactivity of the Fp end group, PFpP amphiphiles were produced via an MIR coupling reaction with oligoethylene phosphine ($CH_3(CH_2)_9P(Ph)_2$). The success of the coupling reaction was proved by $^1$H NMR analysis (Figure S7) and further verified by their micellization behavior due to the amphiphic nature of the resulting molecules. In the mixed solvents of hexane/THF (85/15 by volume), spherical aggregates with fairly uniform size ($R_h$ = 245 nm, PDI = 0.12) were formed as shown by TEM and DLS analysis (Figure S8).

In summary, we have developed a new concept of migration insertion polymerization (MIP) via bulk polymerization of cyclopentadienyldicarbonyldiphenylphosphinopropyliron (FpP). As a result, a new type of MCP, namely PFpP, was invented. The structure of PFpP consists of asymmetric iron units linked by both phosphine coordination and metal−acyl bonds. The polymer also displays narrow molecular weight distributions and is soluble in many organic solvents. The reactivity of the Fp end group has been used for the synthesis of oligoethylene functionalized PFpP. As MIR is a widely used and well-studied organometallic reaction, the polymerization concept of MIP opens up new possibilities to incorporate various metal elements into a novel type of macromolecule chain for functional material exploration.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, IR, $^1$H NMR, $^{13}$C NMR, and $^1$H−$^1$H COSY and $^1$H−$^{13}$C HMQC 2D NMR for the monomers and polymers; $^1$H NMR, TEM image, and DLS result for PFpP amphiphiles and their assemblies. Experiments testing PFpP end group reactivity and monomer solution behavior. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

Xiaosong.wang@uwaterloo.ca

### Author Contributions

†These authors contributed equally.

### Notes

The authors declare no competing financial interest.

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