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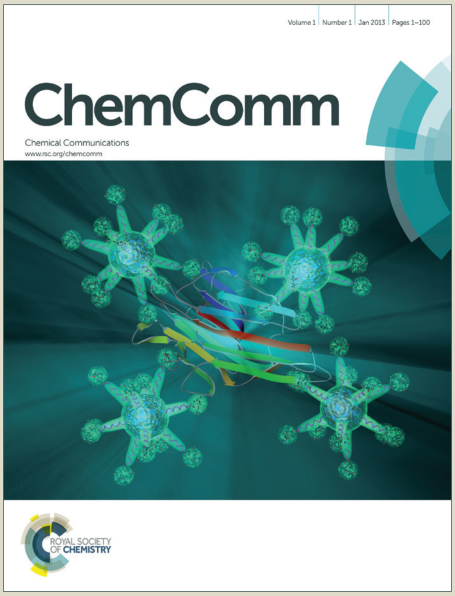

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ARTICLE TYPE

Organometallic Macromolecules with Piano Stool Coordination Repeat Units: Chain Configuration and Stimulated Solution Behaviour

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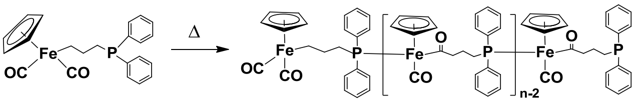
Theoretical calculation illustrates that organometalic macromolecules with piano stool coordination repeat units (Fe-acyl complex) adopt linear chain configuration with a P-Fe-C backbone surrounded by aromatic groups. The macromolecules show molecular weight-dependent and temperature stimulated solution behaviour in DMSO.

Incorporating metal coordination complexes into polymeric backbones[1] is a fundamental approach to alter chain configuration and chemical composition of macromolecules for material innovation.[2] For example, well-understood geometric structures of metal coordination chemistry have been explored for creating novel topologies and microstructures that cannot be achieved with conventional carbon-based polymers.[3] Coordination of metals with rigid multidentate ligands has led to numerous porous networks,[4] cages,[5] and cyclic molecules[6] as a result of directional metal-ligand bonding. On the other hand, processable metal-containing polymers (MCPs), analogues of conventional organic polymers, can be produced via the polymerization of organometallic monomers.[1, 7] Using the synthetic strategies developed for organic polymers, linear[1], dendrimeric[8] and cyclic[9] MCPs have been prepared.

In contrast, the influence of metal complex geometry on the structure of MCPs is virtually unexplored despite its theoretical interest and promise for the variation of polymer chain configuration leading to innovative materials with useful polymer properties. The ignorance of this crucial research issue is mainly attributed to the challenges in main chain MCPs synthesis and characterization. Current polymerization techniques allow limited types of organometallic monomers, such as strained sandwich compounds,[1a, 1d, 1f-j] to be polymerized and result in MCPs stable enough for detailed characterization. It is therefore highly desirable to harness catalysis-oriented organometallic research for possible innovation in polymerization techniques.[10] This effort will offer possibilities to incorporate organometallic coordination units with various geometries into MCPs.

We recently developed migration insertion polymerization (MIP) (Scheme 1).[11] FpP (FpP: $CpFe(CO)_2(CH_2)_3PPh_2$), bifunctional molecules containing cyclopentadienyldicarbonyl (Fp) and tethered phosphine groups, were used as monomers. The crystal structure of FpP shows the monomer adopting a typical three-leg piano stool coordination geometry in which the Cp ring occupies three coordination sites as the seat of the chair.[12] The tethered phosphine group is able to coordinate with an Fe atom via a migration insertion reaction (MIR). As a result of intermolecular MIR, macromolecular backbones with both P-Fe coordination and Fe-C bonds have been created.[11] Since the bond angle of P-Fe-C for Fp acyl derivatives is ca. 90 °C as reported in literature,[13] it would be expected that the MIP of FpP might lead to nonlinear topologies and/or macromolecular cyclic molecules.[14] However, as characterized by both ^1H and ^{31}P NMR, PFpP oligomers possess Fp and phosphine as end groups,[11] suggesting that the polymer may adopt a linear structure. This counterintuitive result promotes exploration of the structure of these polymers in an attempt to understand how the piano stool metal coordination repeat units are connected to form macromolecules and why cyclic reactions are unfavoured. As a newly developed polymerization technique, it is also interesting to investigate whether MIP can be manipulated for the synthesis of higher molecular weight polymers and how the properties of PFpP are influenced by its molecular weight.



Scheme 1 Migration insertion polymerization (MIP) of $CpFe(CO)_2(CH_2)_3PPh_2$, FpP

In this Communication, the combination of density functional theory (DFT) calculations and experimental work indicates that the intramolecular cyclic reaction was unfavoured during MIP. The linear connections of the piano stool metal complex repeat units result in a novel polymer structure which has a metal and phosphorus-containing backbone surrounded with aromatic groups, except for the terminal and penultimate repeat units. PFpP with a relatively high molecular weight (up to 25,700 g/mol) has been produced at 105 °C in the presence of DMSO. The resulting PFpP exhibit molecular weight dependent and temperature dependent solution behaviour, a property that is rarely reported for organometallic polymers.

The first step of the investigation was to understand the reactivity of the two terminal groups (Fp and phosphine) in the PFpP oligomers. To accomplish this, PFpP (degree of polymerization (DP) = 7) was reacted with PPh_2C_6 (PPh_2C_6: hexanyldiphenylphosphine). The reactants and products were examined using ^{31}P NMR spectroscopy. As shown in Figure 1a, the chemical shift at 72.7 ppm (P_1 in Figure 1a), due to the coordinated phosphorus in the chain end repeating unit containing unreacted Fp, disappeared upon reaction, suggesting that the Fp end group is reactive.[11] Figure 1b shows that the signals for the uncoordinated phosphorus from PPh_2C_6 and PFpP's phosphine chain end are distinguishable, appearing at -16.6 (P_0 in Figure 1b) and -16.7 (P_3 in Figure 1b) ppm, respectively. After the reaction, the intensity for the peak at 16.6 ppm resulting from PPh_2C_6 disappeared, while the peak at 16.7 ppm due to PFpP's phosphine end group remained unchanged. This result suggests that PFpP phosphine end group is less reactive as compared to PPh_2C_6. The reactivity of the Fp end group is also verified via ^{1}H NMR of the oligomers. As illustrated in Figure 1c, the signal at 4.7 ppm (Cp_1 in Figure 1c) due to the Cp in the Fp end group upfield shifts to 4.3 ppm (Cp_2 in Figure 1c) as a result of the PFpP end group MIR.[15] On the other hand, the lack of reactivity for the phosphine end group was further verified via the reaction between PFpP and FpMe (FpMe: $CpFe(CO)_2CH_3$) in DMSO-d_6. ^{1}H NMR analysis of the reaction solution shows no evidence that migration insertion reactions occurred (Figure S1), suggesting that the PFpP phosphine end groups are not reactive toward either Fp end groups or FpMe small molecules under the conditions of the experiment. The attenuated reactivity of phosphine end groups can therefore be a reason accounting for the lack of cyclic molecules.

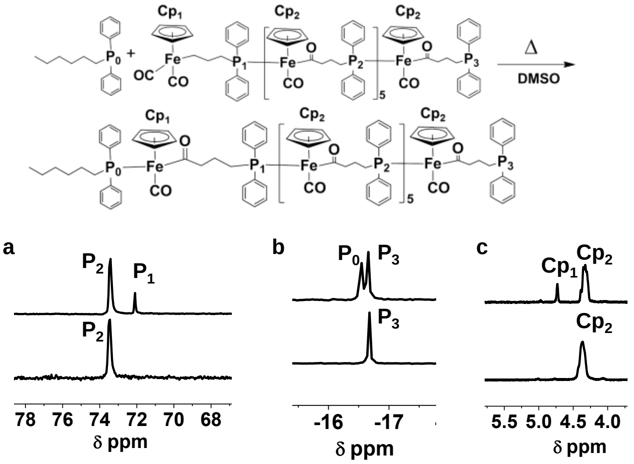


Fig.1 ^{31}P NMR of PFpP solution in the presence of hexanyldiphenylphosphine before heating (above) and after heating for 44 h (below) (a, b); ^{1}H NMR of oligomer PFpP (above) and the hexanyldiphenylphosphine functionalized PFpP (below) in DMSO-d_6 (c).

MIP polymerization was further investigated via computer modeling. DFT calculations were performed on monomeric, dimeric, and trimeric oligomers using the LanL2DZ basis set and the LSDA method. The HOMO/LUMO energy gap drops from 2.86 eV for the monomer to 1.78 eV for the dimer and 1.44 eV for the trimer. Further study was also performed on the dimer, where the energy of planar geometry within the carbon backbone was compared to that of gauche helical geometry. It was found that the HOMO/LUMO gap energy (0.15 eV lower) as well as the overall energy (0.01 eV lower) were lower for the gauche helical conformation. When molecular orbital diagrams of the HOMO and LUMO for the dimeric and trimeric systems are examined (Figures 2, 3), an interesting pattern emerges. Molecular orbitals are localized to each of the FpP units in the dimer. It can be seen from the gauche helical conformation of the dimeric oligomer that the HOMO orbital extends from the Fe center towards the end phosphorus. The trimeric oligomer shows that the HOMO/LUMO orbitals are located on the two termini, skipping the central FpP unit. The HOMO is located towards the phosphine end of the molecule; conversely the LUMO is located on the Fp end. The separation of HOMO/LUMO orbitals prevents effective electron hopping, which may explain that the polymer solution absorbs light at a lower wavelength, 350 nm, with a molar extinction coefficient of 1.13×10^4 L mol^{-1} cm^{-1} (Figure S2).

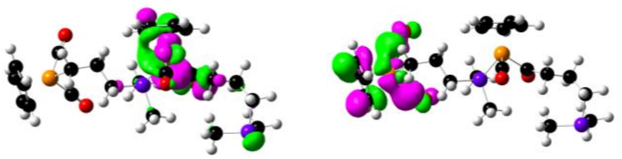


Fig.2 Calculated HOMO (right) and LUMO (left) of dimer with GH geometry.

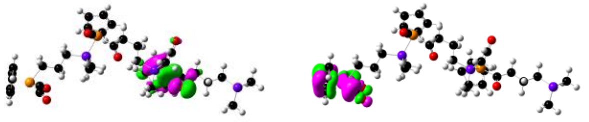


Fig.3 Calculated HOMO (right) LUMO (left) of trimer with TP geometry

Larger oligomeric systems, containing 4, 5, 6 and 11 FpP units, were modeled using a PM6 semi-empirical method. These calculations show a trend towards a linear structure in the longer polymeric chains, while the terminal and penultimate units are seen in the gauche helical conformation relatively to the linear chains (Figure 4a and Figure S3). As shown in Figure 4a, the side view of the macromolecules indicates an alternating opposite alignment of FpP repeat units, with the Cp moieties completely eclipsed. This alignment (except the terminal and penultimate FpP units) is more obvious from top-view images (Figure 4b). As shown in Figure 4b, the Cp rings for FpP repeat units (except the first and the second units) are aligned at two sides of the P-Fe-C main chain, while the substituted groups on the phosphorus are packed on the other two sides. On the basis of the computer modeling, PFpP with piano stool metal coordination repeat units adopts a unique chain configuration with a P-Fe-C backbone surrounded by aromatic groups (Figure 4c). When the bond lengths in the simulated PFpP are compared to those in small molecular Fp acyl derivatives, all coordination bonding distances are shorter (Table S1), especially for Fe-COR, with a bond length 0.11 Å shorter than in $CpFe(CO)(PPhMe_2)C(O)Me$.[13] The decreased bond distance in the polymer explains why PFpP is stable up to 180 °C,[11] while decarbonylation occurs at 110-120 °C for the Fp acyl derivatives.[16]

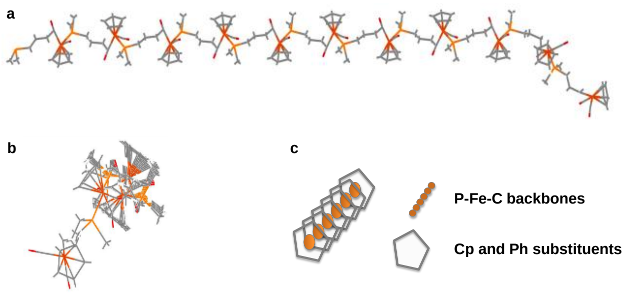


Fig.4 Side view for simulated PFpP with DP=11 (a); top view for simulated PFpP (b); cartoon features the polymer structure (c).

Comparing the oligomeric systems with 5 and 6 FpP units, it is clear that upon the addition of one FpP unit to a 5-mer, the conformation of the terminal and penultimate FpP units will be adjusted. As a result, the Cp for the penultimate FpP will rotate 80° and follow a linear alignment with the remaining FpP units in the chain. The newly added terminal FpP shows a deviation from this trend as it bends ≈150° (measured from the last Fp through the third FpP to the fifth FpP from the end). These structural features are notably prevalent even when the chain is prolonged to eleven FpP units, suggesting that the chain is propagated in a linear fashion. Moreover, the simulation also indicates that the formation of small molecule rings (i.e. 3, 4, or 5 membered rings) is unfavorable with linear geometries prevailing. This result is in agreement with our experiments.

The linear growth of the polymer provides possibilities to prepare PFpP with higher molecular weights. To explore this possibility, the effects of temperature and the presence of DMSO on the polymerization were investigated. The molecular weight of the resulting polymers was either estimated by end group analysis (for low DP samples) or GPC (for high DP samples). The results are listed in Table 1. When the polymerization temperature (70 °C) was lower than the T_g of PFpP (ca. 99 °C)[11] the polymer became vitrified during the polymerization, resulting in PFpP oligomers (entry 1 in Table 1). To address this issue, the polymerization was performed at 105 °C in bulk. As a result, GPC analysis reveals that the resulting polymer has a number-average molecular weight (M_n) of 8200 g/mol with a PDI of 1.35. By comparing ^{31}P NMR spectra for crude products produced at 70 and 105 °C, it was confirmed that the relatively higher molecular weight resulted from enhanced step growth reactions of FpP dimers and oligomers at the higher polymerization temperature, due to increased mobility of the molecules (Figure S4).

Table 1 Effect of temperature and DMSO on the polymerization of FpP in bulk^a

Entry	Temp. (°C)	DMSO^b	Mn (g/mol)	PDI
1	70	--	2800^c	--
2	105	--	8200^d	1.35
3	70	DMSO	3000^d	3.15
4	105	DMSO	25700^d	1.73

^{a} Polymerization time was 20 hours. ^{b} DMSO (ca. 5% by weight) was added. ^{c} end group analysis. ^{d} GPC results: conventional calibration using PS standards for entries 2 and 3, as the samples did not scatter enough light to yield reliable light scattering data; triple detection used for entry 4.

It has been reported that DMSO can induce MIR via coordination to Fe, and a solvent-coordinated intermediate was revealed via ^{1}H NMR analysis in a previous report.[17] We therefore performed MIP of FpP in the presence of a small amount of DMSO (ca. 5% by weight). When the polymerization was performed at 70 °C (entry 3 in Table 1), the molecular weight for the resulting polymers remained low. However the molecular weight distribution was broad (PDI = 3.15) and the weight-average molecular weight (M_w) was 9400 g/mol, suggesting that a small amount of higher molecular weight polymer was produced. This result suggests that DMSO is exerting an influence on MIP, but this effect is limited due to the lower chain mobility at 70 °C. To overcome this limitation, polymerization in the presence of DMSO was performed at 105 °C. GPC analysis of the resulting polymer revealed that the polymer had a M_n of 25,700 g/mol with a PDI of 1.73 (entry 4 in Table 1). Comparing the molecular weight for the polymers produced at 105 °C with and without DMSO (Table 1), it becomes obvious that DMSO can promote step growth coupling, leading to PFpP with relatively higher molecular weights. ^{31}P NMR of the resulting polymers shows that, in addition to the peak at 73 ppm due to the main chain coordinated phosphine, there is a chemical shift at 35 ppm (Figure S5). This peak is attributed to an oxidized phosphine end group.[18] The relatively strong intensity observed for the oxidized phosphine end group is attributed to its faster ^{31}P relaxation time.[18] The appearance of the signal for the oxidized phosphine end group suggests that the polymer chain is linear (note: MALDI-TOF-MS was attempted, but desorption of polymer from the matrix was not observed). Triple detection GPC analysis of the sample (entry 4 in Table 1) also reveals that the α-value of the polymer for the Mark–Houwink equation is 0.53, suggesting that the polymers are approaching theta conditions in THF at 35 °C.

Interestingly, we observed molecular weight-dependent solution behaviour for PFpP in DMSO. Although PFpP oligomer (M_n = 2800 g/mol) is readily soluble, the higher molecular weight PFpP (M_n = 25700 g/mol) is almost completely insoluble in DMSO at 25 °C but solubilizes above 50 °C. Figure 5 shows that this temperature-dependent solubility is reversible, with an upper critical solution temperature (UCST) appearing at 40.3 °C upon heating and at 34.9 °C upon cooling. In contrast, such thermoresponsive solution behavior was not observed for the oligomer PFpP (Figure 5). It is worth noting that polymers, especially organometallic macromolecules, exhibiting molecular weight-dependent UCST in organic solvent are rarely reported.[19] Further research into this property will open up new opportunities for functional materials.

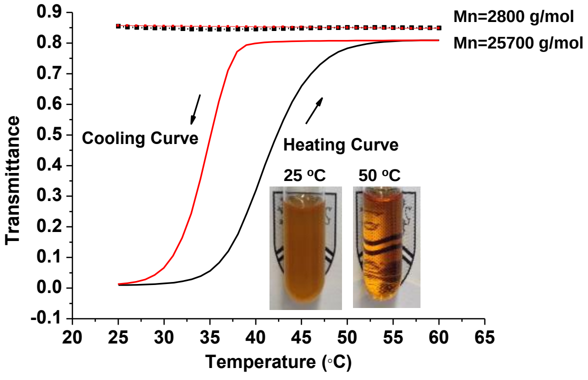


Fig.5 Turbidity curve of PFpP solution in DMSO (4% by weight) at heating and cooling rates of 1 °C/min

Conclusions

In summary, PFpP created by migration insertion polymerization (MIP) of $CpFe(CO)_2(CH_2)_3PPh_2$ (FpP) allows the repeat units with a piano stool geometry to be connected. The resultant polymers possess backbones constructed from P-Fe-C bonding and surrounded with aromatic groups (Cp and Ph). No macromolecular cyclic reactions occurred during MIP due to the attenuated reactivity of the phosphine end groups. Linear polymers with M_n up to 25,700 g/mol have been produced due to increased chain mobility and reactivity of Fp end groups via conducting MIP at 105 ^oC in the presence of DMSO. The resulting PFpP displays molecular weight-dependent solubility. Higher molecular weight PFpP exhibits reversible temperature-dependent solubility in DMSO. This solution behaviour may render these polymers interesting for materials applications, e.g. as positive e-beam resist for lithography,[20] and temperature-stimulated supramolecular organometallic materials.[21]

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Notes and references

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† Electronic Supplementary Information (ESI) available: [^1H NMR, ^{31}P NMR, UV adsorption spectra and simulation results]. See DOI: 10.1039/b000000x/

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