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Flexibility and Stability of Metal Coordination Macromolecules

Heyan Jiang,^[a,b] Diya Geng,^[a] Dapeng Liu,^[a] Nicholas Lanigan,^[a] and Xiaosong Wang*^[a]

Dedication ((optional))

Abstract: The effect of chain structure on flexibility and stability of the macromolecules containing weak P-Fe metal coordination bonds is studied. Migration insertion polymerization (MIP) of FpC_xFp (1) and PR₂C_YPR₂ (2) (Fp: CpFe(CO)₂; C_x and C_y: alkyl spacers; P: phosphine; R: phenyl or isopropyl) generates P(1/2), in which the P-Fe and Fe-P bonds with opposite bonding direction are alternatively arranged in the backbone. On the other hand, P(FpC_xP) synthesized from AB-type monomers (FpCxP) has P-Fe bonds arranged in the same direction, P(1/2) is more rigid and stable than $P(FpC_xP)$, which is attributed to the chain conformation resulting from the P-Fe bonding direction. In addition, the longer spacers render P(1/2)relatively flexible; the phenyl substituents, as compared with the isopropyl groups, improves the rigidity, thermal and solution stability of P(1/2). It is therefore possible to incorporate weak metal coordination bonds into macromolecules with improved stability and adjustable flexibility for material processing.

Introduction

Although various metal containing polymers (MCPs) have been created,^[1-8] It remains difficult in the synthesis of main-chain MCPs,^[6, 9-10] particularly those containing relatively weak metal coordination bonds.^[11-13] To overcome this difficulty, it is necessary to explore backbone structure-correlated physical properties, particularly thermal- and solution stability, but rarely reported.

Among various reported MCPs, the physical properties of polyferrocenylsilane (PFS) as a function of its chemical structure have been thoroughly investigated.^[14] The resultant knowledge has prompted the creative applications of PFS polymers as unique building blocks for functional materials and supramolecular science.^[15-18] On the other hand, the structure-correlated properties of other MCPs, e.g. metal carbonyl polymers, containing relatively weak metal coordination bonds are rarely investigated.^[11-13]

Migration insertion polymerization (MIP) of FpP (Fp = CpFe(CO)₂, P = phosphine) derivatives, AB-type monomers, has generated P(FpP) that is a main chain MCP containing P-Fe coordination bonds (Scheme 1).^[19-20] P(FpP) solids and aggregated colloids in water are air-stable,^[21] whereas, in a good solvent, such as THF, P(FpP) decomposes in a few days.^[19]

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Nevertheless, the stability is sufficient for molecular weight characterization,^[19] material processing^[22] and self-assembly.^[21] This marginal stability is also an opportunity for us to investigate the effect of macromolecular structure on the stability of the metal carbonyl polymers with P-Fe bonds. The resultant knowledge is desirable for the design and creation of MCPs with weak metal coordination bonds.



Scheme 1. Migration insertion polymerization (MIP) of FpC_xP for P(FpC_xP).

The backbone of P(FpP) with P-Fe coordination bonds separated by aliphatic spacers is reminiscent of that for polyamide known as nylon. It is well known that the properties of nylon are related to the direction of amide bonds along the chain. Nylon 66 with reversed direction of the amide bond between each repeating unit favors more hydrogen bonding as compared to nylon 6 prepared from caprolactam in a head-to-tail fashion. Consequently, nylon 66 has higher melting temperature, higher crystallinity, and lower permeability, etc.^[23]

Inspired by this well-known organic system, P(1/2) was synthesized from MIP of $FpC_XFp(1)$ (C_X = alkyl spacers, X = 3 or 6) and $PR_2C_YPR_2$ (2) (R = phenyl or isopropyl, C_Y = alkyl spacers, Y = 3 or 6) (Scheme 2). P(1/2) backbones contain reversely directed P-Fe and Fe-P bonds along the chain. The thermal and solution properties of P(1/2) were studied and compared with those for $P(FpC_XP)$ macromolecules with P-Fe bonds arranged in the same direction (Scheme 1).



Scheme 2. Migration insertion polymerization (MIP) of 1 and 2 for P(1/2).

The manuscript is organized in two sections: 1) Following the synthesis and characterization of P(1/2) macromolecules, their structure-correlated properties are discussed; 2) The effect of P-Fe bonding directions on the properties of P(FpP) and P(1/2) macromolecules are evaluated and discussed. The work illustrates that the relatively weak P-Fe coordination bonds can be incorporated into MCPs with adjustable flexibility and enhanced stability.

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Results and Discussion

Synthesis, characterization and properties of P(1/2). 1 and 2 were synthesized^[24-26] and used as AA and BB-type monomers for MIP (Scheme 2). Upon the polymerization, the oil-like monomers turned to reddish brown solids, which were dissolved in THF and subsequently precipitated in hexane generating yellow powders. The resultant P(1/2) is soluble in a broad range of organic solvents, including THF, CH₂Cl₂, toluene and stable up to more than 10 days in non-chlorinated solvents (Figure S1). In CHCl₃ and CH₂Cl₂, P(1/2) decomposes in one and three days, respectively (Figure S1). (P(1a/2c) and P(1b/2c)) with isopropyl phosphine groups are less stable than those with phenyl phosphine (P(1a/2a), P(1a/2b), P(1b/2a), P(1b/2b)) (Figure S2). This difference suggests that the stability of P(1/2) is not simply a result of the steric impediment around the Fe-P unit, because the isopropyl substituent is much more sterically demanding than the phenyl group. The nature of rigid aromatic structure with a quadrupole moment may also account for the improved stability of P(1/2) with phenyl groups.

NMR and IR analyses indicate that P(1/2) contains the same metal coordination units as P(FpP) polymerized from FpP, ABtype monomers. The spectra for P(1a/2a) are illustrated in Figure 1. As shown in the figure, the ³¹P NMR spectrum shows one signal at 74 ppm due to the coordinated phosphine (Figure 1a) and the ¹H NMR spectrum displays a resonance at 4.19 ppm due to the Cp in Fp acyl units (Figure 1b). The appearance of these two signals suggests that the polymer contains phosphinecoordinated Fp acyl building structures resulted from the MIP.^{[19-} ^{20]} The presence of terminal and acyl CO groups are confirmed by IR spectrum that displays two absorptions at 1911 and 1602 cm⁻¹ (Figure S3a).^[19-20] Correspondingly, ¹³C NMR spectrum reveals two signals at 220 ppm and 274 ppm due to the CO group^[20] (Figure S3b). A weak signal at 34 ppm due to the oxidized phosphine is observed in the ³¹P NMR spectrum (Figure 1a), suggesting that the product contains an uncoordinated phosphine end group.^{[20] 1}H NMR spectrum also reveals a weak signal at 4.68 ppm due to the Cp in Fp end group (Figure 1b).^[27] The number average molecular weight (M_n) for P(1/2) is therefore calculated via end-group analysis and listed in Table 1.



Figure 1. (a) ³¹P and (b) ¹H NMR spectra for P(1a/2a)

The M_n of P(**1**/2) relative to polystyrene (PSt) standards was also characterized by GPC. By comparing the M_n measured by GPC with those estimated from the end group analysis, it appears that the GPC analysis underestimates the M_n ,

particularly for the P(**1/2**) with a larger M_n (entry 1, 3, 5, 6 in Table 1). We reported before that the M_n for P(FpP) measured by GPC coincidently matched that estimated by ¹H NMR end group analysis.^[19, 20] It implies that the chain for P(**1/2**) has a higher degree of contraction resulting in a relatively smaller hydrodynamic volume as compared with P(FpP) chains.

As shown in Table 1, when the polymerization of **1a/2a** is prolonged from 20 h (entry 1) to 80 h (entry 2), there is no substantial increase in M_n . However, the PDI narrows from 1.80 to 1.35 (entries 1, 2). This result can be rationalized by the steric effect. The end groups in the oligomers are relatively reactive for the growth, while the growth of larger molecules ceases due to the steric hindrance. Consequently, a longer polymerization time levels the M_n off resulting in a narrow PDI (entry 2). Similar phenomenon was also observed for other systems.

Table 1. Molecular weights and thermal properties for P(1/2) prepared from migration insertion polymerization of 1 and $2^{[a]}$

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Entry	Monomers	Yield	Mn(GPC ^[b] /NMR ^[c])	PDI	T _{dec}	Tg	
		(%)	K _g /Mole		(°C)	(°C)	
1	1a/2a	82	11.3/18.4	1.80	187	133	
2 ^[d]	1a/2a	93	14.0/-	1.35	-	-	
3	1a/2b	64	7.2/12.1	1.62	182	105	
4	1a/2c	79	2.9/3.7	1.71	169	86	
5	1b/2a	75	12.8/23.1	1.53	189	111	
6	1b/2b	65	4.4/7.7	2.13	182	98	
7	1b/2c	55	2.2/2.4	1.95	160	45	

 $^{[a]}$ Polymerization was performed for 20 h and $^{[d]}$ 80 h in THF at 70 °C, $^{[b]}$ M_n relatively to polystyrene standards, $^{[c]}$ M_n estimated from 1H NMR end group analysis.

The effect of monomer structure on M_n of P(1/2) obtained under the same conditions is discussed. As shown in Table 1, both P(1a/2c) and P(1b/2c) have a very low M_n (entries 4, 7), which is rationalized by the larger steric effect of 2c with isopropyl groups. The length of the spacers in the monomers also significantly influences the M_n . For example, the M_n for P(1a/2a) with propyl spacers (entry 1) is obviously larger than that for P(1b/2b) with hexyl spacers (entry 6). We have found this relationship in our previous research. MIP of FpC₆P with a hexyl spacer only generated P(FpC₆P) oligomers;^[29] while P(FpC₃P) with a relatively larger M_n was produced under the same conditions.^[19] The flexible backbone resulting from the longer spacer may reduce the possibility for the end groups to encounter each other for intermolecular metal coordination reactions.

The thermal properties of P(**1**/**2**) was analyzed using DSC and TGA. Within the range of M_n achievable by MIP, the variation of T_g as a function of M_n is negligible. For example, we observed that P(FpC₃P) molecules with degree of polymerization (DP) of 7 and 20 have the same T_g of 99 °C.^[19, 20] So the difference in T_g for P(**1**/**2**) as listed in Table 1 is attributed to the variation in chemical structure. In general, the polymers with phenyl groups and shorter spacers, such as P(**1a**/**2a**), are more rigid with a higher T_g. The onset of decomposition temperature (*T*_{dec}) for P(**1**/**2**) is in the range from 160-190 °C (Table 1 and Figure S5), which is 40-70 °C higher than the *T*_{dec} for Fp acyl small

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molecules,^[31-32] As shown in Table 1, the substituent groups on the phosphorus influence the thermal stability more than the spacers. The T_{dec} for P(**1a/2c**) and P(**1b/2c**) containing isopropyl phosphine groups is ca. 160 °C and 169 °C (entries 4 and 7), respectively, while the T_{dec} is in the range between 180 °C and 190 °C for all the polymers with phenyl phosphine groups (entries 1, 3, 5, 6). The effect of the spacer length on the T_{dec} for these polymers (entry 1, 3, 5, 6) is within 10 °C.

The effect of P-Fe bonding direction along the chain. P(1a/2a)/P(FpC₃P) and P(1b/2b)/P(FpC₆P) are two pairs of macromolecules with three and six carbon atoms in the spacers, respectively. Although the macromolecules for each pair have the same chemical composition, the direction of P-Fe coordination along the backbone is different in a way reminiscent of the amide bonds in nylon 66 and nylon 6. This difference in the backbone structure affects the thermal properties of the macromolecules. As shown in Table 1, the T_{g} for the former polymer in the pairs is 133 °C (P(1a/2a)) and 98 °C (P(1b/2b)), respectively. The corresponding counterpart has a T_g of 99 °C (P(FpC₃P))^[19] and 68 °C (P(FpC₆P)),^[29] respectively. This difference in T_g (ca. 30 °C) suggests that the reversed direction of P-Fe bond between each repeating unit renders P(1a/2a) and P(1b/2b) more rigid. As the T_{dec} is compared, P(1a/2a) (187 °C) and P(1b/2b) (182 °C) are relatively stable than P(FpC₃P) (180 °C)^[19] and P(FpC₆P) (170 °C),^[29] respectively. The enhanced thermal stability for P(1/2) may be related to the chain conformation resulting from the metal coordination direction in the backbone.

 $P(FpC_xP)$ (X = 3, 6) with P-Fe bonds arranged in the same direction along the chain is expected to have a more regular structure. Dynamic simulation has indicated that $P(FpC_xP)$ backbones are fully extended into a linear helical conformation in THF.^[30] P(1/2) with opposite direction of P-Fe bonds between each coordination unit may adopt a non-linear conformation (Scheme 3). The less ordered chain conformation may reduce the possibility for the relatively weak metal coordination bonds to interact with the external media (Scheme 3), which is a possible reason for the improved stability of P(1/2).



Scheme 3. Schematic representation of the chain conformation for $P(FpC_3P)$ and P(1a/2a).

To test this speculation, we examined the solution stability of P(**1a/2a**) in THF using ³¹P NMR and GPC. After exposing to air for 20 days, the ³¹P NMR spectrum (Figure 2a) shows no change in the signals. GPC analysis further indicates that there is no degradation of the sample and the M_n remains unchanged (Figure 2c). 30 days later, the ³¹P NMR spectrum displays multiple signals in addition to those due to the original P(**1a/2a**), suggesting the occurrence of the decomposition. So **P(1a/2a**) is stable for at least 20 days in THF. In contrast, P(FpC₃P) in THF, as we have reported before, decomposed resulting in precipitates in a few days.^[19] The ³¹P NMR of the supernatant shows weak signals (Figure 2b) corresponding to the decomposed fragments with low molecular weight as indicated by GPC analysis (Figure 2c). Similarly, P(**1b/2b**) also has a higher solution stability than P(FpC₆P) (Figure S6).



Figure 2. Time-resolved ³¹P NMR spectra (a) for the THF solution (2 mg mL⁻¹) of P(**1a/2a**); (b) and P(FpC₃P); (c) GPC curves for P(**1a/2a**) after aging in THF for 20 days and for P(FpC₃P) after aging in THF for 10 days.

If the stability is indeed caused by the chain conformation, photo- and oxidant-induced degradation behavior should be different. Photons can penetrate through the solution and polymers for the degradation reaction regardless of the chain conformation. Figure 3 and S7 illustrate the time-resolved ³¹P NMR spectra for the solutions of P(**1**/**2**) and P(FpC_xP) in THF exposed to an LED light (wavelength: 400–410 nm). As shown in the figures, the degradation behavior for both P(**1**/**2**) and P(FpC_xP) is similar. After 10 minutes, the intensity for the peak due to the main chain coordinated phosphine at 74 ppm obviously decreases. One hour later, this signal is barely visible suggesting that all macromolecules decompose.



Figure 3. Time-resolved ³¹P NMR spectra for (a) P(**1a/2a**) and (b) P(FpC₃P) in THF (5 mg mL⁻¹) irradiated by LED light (wavelength = 400–410 nm).

The time-resolved ³¹P NMR spectra for P(1a/2a) and P(FpC₃P) in the presence of H₂O₂ are illustrated in Figure 4. As shown in Figure 4a, although the intensity for the signal due to the oxidized phosphine increases slowly over a day, substantial amount of the coordinated phosphine in P(1a/2a) with chemical shift at 74 ppm remains. Not until the fourth day do we start to observe the precipitates (Figure S8). On the other hand, $P(FpC_3P)$ in the presence of H_2O_2 decomposes and generates precipitates in three hours (Figure S8). Consequently, the ³¹P NMR of the solution shows a weak signal due to the coordinated phosphine at 74 ppm (Figure 4b). The ³¹P NMR spectra also indicate that P(1b/2b), as compared with P(FpC₆P), are more resistant to H₂O₂ (Figure S9). This difference in the resistance can be attributed to the conformation of chains. The linear helical structure of PFpC_xP backbone^[30] expels the iron coordination units towards the solvent and therefore enhances the interaction between H_2O_2 and the metal coordination units. In contrast, the metal coordination units in P(1/2) may be embedded within the less regular chains, which reduces the possibility to react with H₂O₂ and thus enhances the stability.



Figure 4. Time-resolved ³¹P NMR spectra for (a) P(**1a/2a**) and (b) P(FpC₃P) in THF (10 mg mL⁻¹) in the presence of H_2O_2 (30 %).

The macromolecules are constructed from the same metal coordination units that are chiral at the Fe center, so circular dichroism (CD) experiments may be able to probe the difference in the chain conformation. THF solutions of P(**1a/2a**), P(**1b/2b**), P(FpC_xP) (X = 3 and 6) were examined. As shown in Figure 5a and 5b, all the solutions show positive CD signals. Fp heptanoyl compound (FpC₆), representing the Fe coordination units in the

macromolecules, has a similar CD profile (Figure 5 C and 5d). It is therefore reasonable to think that the chiral structure of the metal coordination units in the backbone is responsible for the CD signal and the intensity of the signal for the solutions with the same concentration can be an indicative of the stereoregularity of the backbones. By comparing P(FpC₃P) and P(FpC₆P) with P(1a/2a) and P(1b/2b) respectively, the intensities of the CD signals for the former polymers are higher, suggesting that P(FpC_xP) (X = 3, 6) has a higher ordered chain conformation than P(1/2). This preliminary data illustrate that the directions of metal coordination bonds along the chain affects the chain conformation and is a factor adjusting the stability of the macromolecules with weak Fe-P metal coordination bonds.



Figure 5. Circular dichroism (CD) spectra of (a) $P(FpC_3P)_{20}$ and $P(1a/2a)_{14}$ with the same concentration of Fe ([Fe] = 2.47 x $10^{-3} \mu$ M); (b) $P(FpC_6P)_{14}$ and $P(1b/2b)_5$ with the same concentration of of Fe ([Fe] = 2.24 x $10^{-3} \mu$ M) (c) FpC_6 in THF ([Fe] = 1.91 x $10^{-3} \mu$ M).

Conclusions

Migration insertion polymerization (MIP) of ditopic Fp derivatives, FpC_xFp (1) and bi-functional phosphine, PR₂C_YPR₂ (2) has generated P(1/2). The backbone of P(1/2) is constructed from the alternative P-Fe and Fe-P coordination bonds with opposite bonding directions. In contrast, P(FpC_xP) contains P-Fe bonds in the same direction along the chain. P(1/2) is more rigid and stable than P(FpC_xP), which is rationalized by the less ordered chain conformation of P(1/2) resulting from the opposite direction of the metal coordination bonds along the chain. In addition, the flexibility and stability of P(1/2) can be adjusted by the length of aliphatic organic spacers and the substituents on the phosphorus centres. It is therefore possible to incorporate weak metal-coordination bonds into MCPs for processing materials by adjusting the coordination direction along the chain and the chemical structure of organic ligands.

Experimental Section

Materials and instrumentation. THF was freshly distilled under nitrogen Sodium (K), from Na-benzophenone. (Na), potassium cyclopentadienylirondicarbonyl dimer (Fp₂). 1.3-Bis(diphenylphosphino)propane, 1,6-Bis(diphenylphosphino)hexane, diisopropylphosphine, n-butyllithium, 1,3-dichloropropane and 1.6dichlorohexane were purchased from Strem Chemicals Inc. Benzophenone was purchased from Fisher Scientific. $P(FpC_XP)$ (X = 3 or 6) was prepared according to literature.^[20, 29] All chemicals were used as received unless otherwise indicated.

The molecular weights and molecular weight distributions (M_w/M_n) for P(1/2) macromolecules were characterized by GPC using PSt standards. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹. ¹H, ³¹P, and ¹³C NMR spectra were obtained on a Bruker-300 (300 MHz) spectrometer at ambient temperature using appropriate solvents. NMR samples were prepared under a dry nitrogen atmosphere unless otherwise indicated. Fourier transform infrared (FT-IR) spectra were recorded using a Perkin Elmer Spectrum RX I FT-IR system. The samples were ground with KBr and then pressed into transparent pellets. LED light (wavelength 400-410 nm, Super Bright LEDs Inc.) was used as the light source for the photo-degradation experiments. Differential scanning calorimetry (DSC) data were recorded using a Q10 DSC (TA Instruments) under a flow of N_2 (50 mL min⁻¹). Samples (ca. 5 mg) were enclosed in aluminum pans, with an empty aluminum pan as the reference. The measurements were performed by heating the samples from -50 °C to 155 °C (ramp: 10 °C min-1). The thermal history was removed by a cycle of heating the samples to 155 °C (ramp: 10 °C min⁻¹) and then cooling back to -50 °C (ramp: 10 °C min-1). Thermal gravimetric analysis (TGA) was carried out on a TGA Q50 under N₂ at a heating rate of 10 °C min⁻¹. Samples were dried under vacuum at ambient temperature prior to the measurements. Circular dichroism (CD) spectra were recorded on a Jasco J720 spectrometer (Japan) at 25 °C under N₂. THF solutions of the samples (1 mg mL⁻¹) in a cell with 1.0 cm path length were prepared for the experiments.

Synthesis. All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques unless otherwise indicated. FpC_xFp (1)^[24] and PR₂C_YPR₂, R = isopropyl (2c) were synthesized according to the literature.^[25-26] PR₂C_YPR₂, R = phenyl (2a, 2b) is commercially available;

Synthesis of 1: 1 was prepared via a reaction of CI(CH₂)_xCI (X = 3, 6) with K[CpFe(CO)₂]. A typical experiment process is briefly described. CI(CH₂)₃CI (0.64 g, 5.70 mmol) was added dropwise to a THF solution of K[CpFe(CO)₂] (2.5 g, 11.4 mmol). The reaction mixture was stirred for 15 h at 24 °C and then heated to reflux for 6-8 h. Afterwards, the reaction was cooled to 24 °C and the solvent was removed under a reduced pressure. The residue was extracted with dichloromethane (50 cm³). The resulting solution was filtered and the solvent was removed under reduced pressure leaving a brown oil. Addition of hexane (20 cm³) to the oil and cooling in fridge caused a rapid formation of yellow crystals. Recrystallization of these crystals from hexane yielding the required products as yellow plates. FpC₃Fp: yield 54%. ¹H NMR (CDCl₃): 4.72 ppm (s, 10H, C5H5), 1.46-1.45 ppm (m, 6H, CH2CH2CH2); FT-IR (Nujol mull): 2006 and 1944 cm⁻¹ (terminal CO stretching); FpC₆Fp: yield 45%. ¹H NMR (CDCl₃): 4.73 ppm (s, 10H, C₅*H*₅), 1.54-1.32 ppm (m, 12H, CH₂CH₂CH₂CH₂CH₂CH₂CH₂) FT-IR (Nujol mull): 2006 and 1946 cm⁻¹ (terminal CO stretching) (¹H NMR spectra is illustrated in Figure S10).

Synthesis of 2c: A typical process for the synthesis of **2c** is described. To an ice-cooling suspension of lithium diisopropylphosphide in ether/n-hexane prepared from diisopropylphosphine (7.7 g, 65 mmol) and n-butyllithium (1.6 M, 67 mmol), 1,3-dichloropropane (3.5 g, 31 mmol) was added slowly in the period of 10 min. The resulting mixture was stirred for

10 h at 24 °C and then heated to reflux for 30 min. After cooling, deoxygenated water (25 ml) was added and subsequently the organic layer was separated. The water layer was extracted with ether. The combined organic solution was then dried over magnesium sulfate for a few hours. After filtration, the organic solvents were removed in vacuo. The residue was distilled in vacuo yielding the diphosphine as a colorless liquid, 7.1 g (81%), b.p. 95-98°C / 0.01 mmHg. ¹H NMR (CDCl₃): 1.69-1.65 ppm (m, 4H, CH(CH₃)₂), 1.44-1.42 ppm (m, 4H, CH₂P), 1.22-1.00 ppm (m, 26H, CH₂CH₂CH₂, CH(CH₃)₂). ³¹P NMR (CDCl₃): 3.83 ppm(s) (¹H and ³¹P NMR spectra is illustrated in Figure S11).

Migration insertion polymerization: Migration insertion polymerization 1 and 2 was performed in THF solution (20 wt%) at 70 °C. Samples were withdrawn for ³¹P NMR analysis during the polymerization. 20 h later, the solution was cooled to 24 °C. The crude product was dissolved in a minimum of THF, and then precipitated in hexane. The precipitate was collected and dried under vacuum at room temperature overnight yielding a bright yellow powder. P(1a/2a): ¹H NMR (CDCl₃): 7.30-7.25 ppm (C₆*H*₅), 4.68 ppm (end group Cp, C₅*H*₅), 4.19 ppm (main chain Cp, C₅*H*₅), 2.50-2.35 ppm (COC*H*₂), 1.84-1.09 ppm (CH₂C*H*₂CH₂, CH₂PFe). ³¹P NMR (CDCl₃): 74.1 ppm (backbone PFe) and 34.1 ppm (oxidized end group PPh₂O). FTIR: 1911 cm⁻¹ (terminal CO stretch) and 1602 cm⁻¹ (acyl CO stretching). P(1a/2b): ¹H NMR (CDCl₃): 7.42-7.25 ppm (C₆ H_5), 4.68 ppm (end group Cp, C₅ H_5), 4.31 ppm (main chain Cp, C_5H_5), 2.66-2.25 ppm (COC H_2), 1.55-1.18 ppm (CH₂C H_2 CH₂, CH₂CH₂CH₂CH₂CH₂CH₂, CH₂PFe). ³¹P NMR (CDCl₃): 74.0 ppm (backbone PFe), -13.5 ppm (end group PPh₂), and 34.9 ppm (oxidized end group PPh₂O). FTIR: 1910 cm⁻¹ (terminal CO stretch) and 1602 cm⁻¹ (acyl CO stretching). P(1a/2c) ¹H NMR (CDCl₃): 4.71 ppm (end group Cp, C₅H₅), 4.53 ppm (main chain Cp, C₅H₅), 2.99-2.72 ppm (COCH₂), 2.17-1.11 ppm (CH₂CH₂CH₂, CH(CH₃)₂, CH₂PFe). ³¹P NMR (CDCl₃): 77.8 ppm (backbone PFe) and 54.5 ppm (oxidized end group P(isopropyl)₂O). FTIR: 1911 \mbox{cm}^{-1} (terminal CO stretch) and 1601 \mbox{cm}^{-1} (acyl CO stretching). P(1b/2a): ¹H NMR (CDCI₃): 7.28-7.25 ppm (C₆H₅), 4.69 ppm (end group Cp, C_5H_5), 4.19 ppm (main chain Cp, C_5H_5), 2.66-2.37 ppm (COCH₂), 2.12-0.91 ppm (CH₂CH₂CH₂, CH₂CH₂CH₂CH₂CH₂CH₂CH₂, CH₂PFe). ³¹P NMR (CDCl₃): 73.9 ppm (backbone PFe), -14.3 ppm (end group PPh₂), and 34.1 ppm (oxidized end group PPh₂O). FTIR: 1910 cm⁻¹ (terminal CO stretch) and 1601 cm⁻¹ (acyl CO stretching). P(1b/2b): ¹H NMR (CDCl₃): 7.44-7.30 ppm (C₆*H*₅), 4.68 ppm (end group Cp, C₅*H*₅), 4.33 ppm (main chain Cp, C5H5), 2.80-2.40 ppm (COCH2), 2.30-0.99 ppm (CH₂CH₂CH₂CH₂CH₂CH₂, CH₂PFe). ³¹P NMR (CDCl₃): 73.9 ppm (backbone PFe) and 34.9 ppm (oxidized end group PPh₂O). FTIR: 1908 cm⁻¹ (terminal CO stretch) and 1605 cm⁻¹ (acyl CO stretching). P(1b/2c): ¹H NMR (CDCl₃): 4.70 ppm (end group Cp, C₅*H*₅), 4.53 ppm (main chain Cp, C5H5), 3.02-2.86 ppm (COCH2), 2.16-1.16 ppm (CH2CH2CH2, $CH_2CH_2CH_2CH_2CH_2CH_2, CH(CH_3)_2, CH_2PFe). {}^{31}P NMR (CDCI_3): 77.7$ ppm (backbone PFe) and 54.6 ppm (oxidized end group P(isopropyl)₂O). FTIR: 1909 \mbox{cm}^{-1} (terminal CO stretch) and 1602 \mbox{cm}^{-1} (acyl CO stretching).

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