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Controlled isoprene polymerization mediated by iminopyridine-iron (II) acetylacetonate pre-catalysts

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National Natural Science Foundation of China, Grant/Award Number: 21702215; CAS Hundred Talents Program, Grant/ Award Number: Y5100719AL; Major Science and Technology Innovation Program of Shandong Province, Grant/Award Number: 2018CXGC1105 A ligand controlled stereoselective polymerization of isoprene has been developed. A series of (aryl/alkyl)-iminopyridine iron (II) acetylacetonate complexes: (aryl = Ph Fe1; alkyl = CH₂Ph Fe2, CH (Ph)₂ Fe3, CH (Me)₂ Fe4, C (Me)₃ Fe5, C (Me)₂CH₂C(Me)₃ Fe6), has been prepared in which steric and electronic substituents systematically modified to investigate their influences for isoprene polymerization. The molecular structure of representative complex Fe2 was confirmed by single crystal X-ray diffraction and, revealed a distorted octahedral geometry at iron center. On treatment with methylaluminoxane (MAO), Fe1-Fe6 displayed low (Fe5 & Fe6) to high activities (Fe1-Fe4) with quantitative monomer conversion (>99%) for isoprene polymerization producing polyisoprene of high molecular weight (up to 2.0×10^5 g/mol) and unimodal molecular weight distribution (1.4-3.3). Specifically, complex Fe2 (alkyl = CH₂Ph) displayed the highest activity of 7.0×10^6 g (mol of Fe)⁻¹ h ⁻¹ with 85% conversion of monomer over run time of 10 min at 25 °C. While, Fe6 catalyzed polyisoprene possessed high content of trans-1,4 unit (up to 87%). Furthermore, the influence of the reaction parameters and the nature of the ligands on the catalytic activities and microstructural properties of the polymer were investigated in detail.

KEYWORDS

Iminopyridine ligand, iron (II) acetylacetonate complex, isoprene polymerization

1 | INTRODUCTION

As a valuable alternative material to the natural rubber, polyisoprene has emerged as one of the most promising thermoplastic elastomers in the field.^[1] The excellent processing and recycling properties of these synthetic polymers make them superior over the classical volcanized rubber. These properties can easily be controlled by adjusting the microstructure of the polymer, particularly by controlling the molecular weight and stereoselectivity of the polymer and thus these polymers have found widespread applications ranging from the tire industry,

through shape memory functional materials to medicinal industries. For example, *cis*-1,4 polyisoprene characteristically resemble to the natural rubber being structurally similar, therefore is highly demanded as alternative material for the tire industry.^[2] Meanwhile, *trans*-1,4 polyisoprene is widely used as shape memory functional materials due to having the similar properties to guttapercha rubber.^[3] Considering this industrially valuable material, researchers are engrossed to develop new and efficient methods for controlling the properties of isoprene polymerization. For this homogeneous transition metal complexes have attracted much attention in term 2 of 10 WILEY Organometallic-Chemistry

of high activities and subtle control over the properties of the polymer for olefin polymerization. For the isoprene polymerization, titanium, lithium and rare earth metal based catalysts^[4–7] have been extensively studied in academia as well as in industry. Compared to the early transition metal catalysts or conventional Ziegler-Natta catalysts, few studies are found in which late transition metal complexes used as catalysts for the isoprene polymerization.^[8–10]

The discovery of α -diimine-Pd (II)–/-Ni (II)^[11-23] and bis (phenylimino)pyridine-Co (II)/Fe (II) based catalysts^[24-27] for the polymerization of olefins were found as instrumental in the development in the late transition based catalyst for olefin polymerization. Since then, the well-defined late transition metal complex began to attract attention from scientific researcher in academia as well as from industrial community to use these complexes as catalysts for olefin polymerization, due to their expedient preparation, high reactivity, single catalytic behavior and controlled stereoselectivity. Among them, iron metal based catalyst is an excellent choice because of its low toxicity, low cost, friendly environment and significant natural abundance. However, less attention has given to the iron based catalysts for diene polymerization because of their lower activities and selectivities. Since 1970, studies have focused on the complexing agent to stabilized the active species and prevent them being reduced, but the catalytic activity and selectivity were low.^[28-35] In 2002, Porri and his coworkers disclosed (bipy)₂FeEt₂ complexes as stereospecific catalyst for isoprene polymerization and produced highly selective 3,4 polvisoprene.^[36] Later, Ricci et al. investigated iron (II) chloride catalysts bearing aliphatic and aromatic N,Nbidentate ligand framework for the polymerization of isoprene and other 1,3-dienes. These catalyst displayed high activities and generated polyisoprene with different microstructural properties.^[37] In 2012, the group of Ritter employed iminopyridine Fe (II) chloride complexes in conjunction with methylaluminoxane and $[Ph_3C]$ $[B(C_6F_5)_4]$ as a ternary catalyst system for isoprene and other 1,3-diene polymerization. At very low loading of iron catalysts as low as 0.02% displayed high activity for isoprene polymerization and produced polymer with different microstructure ranging from highly selective trans-1,4 to cis-1,4 polyisoprene.^[38] Elsewhere, Chen group also explored catalytic potential of iminopyridine iron chloride complexes for isoprene polymerization and exhibited moderate cis-1,4 selectivity with high molecular weight.^[39] As part of our on-going project to establish the correlation between the ligand framework and its effect on catalytic performance, we have examined the fluorinated aryl-iminopyridine Fe (II) complexes and systematically studied the polymerization of isoprene by using

binary and ternary catalyst systems. These catalytic systems exhibited high activities with good stereoselectivity and molecular weight.^[40]

Generally, it is noted that counteranion plays key role in regulating the catalytic activity, selectivity and mechanism of transition metal catalyzed reaction.^[41–43] In the previous studies, Fe (acac)₃/additional donor/reducing agent ternary systems have been reported for the isoprene polymerization that exhibited moderate activity and selectivity.^[44-46] With a view to gain deeper insight and to study the effect of auxiliary ligand into the catalytic performance of iminopyridine iron complexes, in this contribution, we reported a series of well-defined iminopyridine iron acetylacetonate catalysts for isoprene polymerization. A detailed polymerization study is performed to investigate the effect of different reaction conditions on catalytic performance and polymer properties. In addition, detail microstructural analysis of obtained polymer is performed by ¹H/¹³C NMR spectroscopy. Herein reported catalysts exhibited substantial enhanced catalytic activities and controlled polymer properties.

2 | EXPERIMENTAL

2.1 | Materials

All experiments were carried out under argon atmosphere by using standard Schlenk techniques or in glovebox. Fe (acac)₂, methylaluminoxane (MAO, 1.5 M solution in toluene), triethylaluminum (AlEt₃, 1.0 M solution in toluene) and triisobutylaluminum $(Al(i-Bu)_3)$ 1.0 M solution in toluene) and starting materials of aldehyde and amines for the synthesis of ligands were purchased and used without further purification. Toluene was refluxed over sodium and distilled and stored over molecular sieves under nitrogen. Hexane and dichloromethane were refluxed over calcium hydride and distilled and stored over molecular sieves under argon conditions. Commercial available isoprene was purchased and purified by distillation over calcium hydride before use. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured by high temperature gel permeation chromatography (GPC) using a PL-GPC 220 chromatography and maintained at 150 °C by using trichlorobenzene as eluent and polystyrene as standard. NMR spectra were conducted on a Bruker Advance 400 spectrometer at 298 K. ¹H NMR and ¹³C NMR spectra of ligands and polyisoprene were recorded in CDCl₃ and trimethylsilane as internal reference. The polyisoprene microstructure of the 1,4 and 3,4 ratio was determined from ¹H NMR of the 1,4 = CH signals at 5.15 ppm and the $3,4 = CH_2$ signal at 4.7 ppm. The

trans/cis-1,4 stereoisomer ratio was determined from ¹³C NMR of the –CH₃ signals of *cis*-1,4 at 23.8 ppm and *trans*-1,4 at 16.3 ppm. Mass spectra for Fe complexes were detected using ACQUITYTM UPLC & Q-TOF MS Premier. Elemental analysis was recorded using Vario EL III elemental analyzer. X-ray diffraction data was performed on Smart 1000 diffractometer with Mo K-alpha X-ray source ($\lambda = 0.71073$ Å) at 150 K. Attenuated total reflection- infrared (ATR-IR) spectroscopy was conducted using Thermo Scientific Nicolet iN10.

2.2 | Synthesis and characterization of ligands (L1–L6)

All the ligands are known and can be prepared using a procedure reported in the literature.^[38] The ¹H and ¹³C NMR spectra of these ligands agreed with reported ones.

2.2.1 | 2-(phenyliminomethyl)pyridine L1

Yellow oil, 2.0 g, 58% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 8.75–8.69 (m, 1H), 8.61 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.84–7.80 (m, 1H), 7.46–7.35 (m, 3H), 7.31–7.27 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 160.6, 154.5, 150.9, 149.6, 136.7, 129.2, 126.7, 125.1, 121.9, 121.1.

2.2.2 | 2-(benzyliminomethyl)pyridine L2

Yellow oil, 2.5 g, 68% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.64–8.63 (m, 1H), 8.49 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.74–7.69 (m, 1H), 7.74–7.69 (m, 6H), 4.87 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 162.9, 154.6, 149.4, 138.7, 136.6, 128.6, 128.2, 127.2, 124.8, 121.4, 65.0.

2.2.3 | 2(diphenylmethyliminomethyl) pyridine L3

White solid, 1.1 g, 75% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 8.58 (d, J = 4.4 Hz, 1H), 8.53 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.67–7.64 (m, 1H), 7.40 (d, J = 7.2 Hz, 4H), 7.31 (t, J = 7.2 Hz, 4H), 7.23–7.20 (m, 3H), 5.70 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ : 162.0, 154.7, 149.3, 143.3, 136.4, 128.5, 127.7, 127.1, 124.8, 121.5, 77.7.

2.2.4 | 2-(isopropyliminomethyl)pyridine L4

Colorless oil, 2.1 g, 68% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 8.61 (d, J = 4.40 Hz, 1H), 8.37 (s, 1H), 7.96 (d,

J = 7.6 Hz, 1H), 7.72–7.70 (m, 1H), 7.29–7.25 (m, 1H), 3.65–3.59 (m, 1H), 1.26 (d, J = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ : 159.3, 154.9, 149.5, 136.6, 124.6, 121.4, 61.5, 24.1.

2.2.5 | 2-(tert-butyliminomethyl)pyridine L5

Colorless oil, 1.2 g, 72% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 8.63–8.62(m, 1H), 8.36 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.74–7.70 (m, 1H), 7.30–7.26 (m, 1H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ : 156.6, 155.7, 149.4, 136.7, 124.5, 121.1, 58.0, 29.7.

2.2.6 | 2-(2,4,4-trimethylpentan-2yliminomethyl)pyridine L6

Light yellow oil, 1.6 g, 80% yield; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.64–8.59 (m, 1H), 8.34 (s, 1H), 8.04–8.02 (m, 1H), 7.74–7.70 (m, 1H), 7.30–7.27 (m, 1H), 1.71 (s, 2H), 1.33 (s, 6H), 0.95 (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 155.9, 155.8, 149.2, 136.6, 124.3, 120.7, 61.6, 56.5, 32.1, 31.8, 29.6.

2.3 | Synthesis and characterization of iron complexes

The corresponding ligand and Fe $(acac)_2$ were added in anhydrous dichloromethane (10 ml) at room temperature. The reaction mixture was stirred for 24 hr at same temperature. After that, reaction mixture concentrated to 2 ml and hexane was then added to induce precipitation and the precipitate collected by filtration, washed with hexane and dried under vacuum to give the corresponding complex.

2.3.1 | 2-(phenyliminomethyl)pyridyliron (II) acetylacetonate Fe1

Brown solid, 75 mg, 44% yield. ATR-IR (cm⁻¹): 1582 ν (C=N), 1514, 1491, 1395, 1257, 1014, 920, 784, 762. TOF-MS-ES+ (*m*/*z*): calcd. For $[C_{22}H_{24}FeN_2O_4]^+$: 436.1085, found: 436.1095. Anal.: calcd. For $C_{22}H_{24}FeN_2O_4$ ·H₂O: C, 58.16; H, 5.77; N, 6.17; found: C, 57.82; H, 5.75; N, 6.15.

2.3.2 | 2-(benzyliminomethyl)pyridyliron (II) acetylacetonate Fe2

Brown solid, 189 mg, 54% yield. ATR-IR (cm⁻¹): 1578ν(C=N), 1511, 1400, 1360, 1014, 921, 773, 763. TOF-

4 of 10 WILEY Organometallic

MS-ES+ (m/z): calcd. For $[C_{23}H_{26}FeN_2O_4]^+$: 450.1242, found: 450.1244. Anal.: calcd. For $C_{23}H_{26}FeN_2O_4 \cdot H_2O$: C, 58.99; H, 6.03; N, 5.98; found: C, 59.18; H, 6.12; N, 5.98. X-ray quality crystals were obtained from slow evaporation of dichloromethane.

2.3.3 | 2-(diphenylmethyliminomethyl) pyridyliron (II) acetylacetonate Fe3

Brown solid, 80 mg, 39% yield. ATR-IR (cm⁻¹): 1581 ν (C=N), 1513, 1449, 1398, 1012, 919, 768, 740, 710. TOF-MS-ES+ (*m*/*z*): calcd. For [C₂₉H₃₀FeN₂O₄]⁺: 526.1555, found: 526.1564. Anal.: calcd. For C₂₉H₃₀FeN₂O₄·H₂O: C, 63.98; H, 5.92; N, 5.15; found: C, 63.62; H, 6.07; N, 5.01.

2.3.4 | 2-(isopropyliminomethyl) pyridyliron (II) acetylacetonate Fe4

Brown solid, 160 mg, 67% yield. ATR-IR (cm⁻¹): 1581 ν (C=N), 1511, 1442, 1394, 1259, 1013, 921, 775,760. TOF-MS-ES+ (*m*/*z*): calcd. For [C₁₉H₂₆FeN₂O₄]⁺: 402.1242, found: 402.1250. Anal.: calcd. For C₁₉H₂₆FeN₂O₄·H₂O: C, 54.30; H, 6.72; N, 6.67; found: C, 55.30; H, 6.12; N, 6.73.

2.3.5 | 2-(tert-butyliminomethyl) pyridyliron (II) acetylacetonate Fe5

Yellow solid, 155 mg, 63% yield. ATR-IR (cm⁻¹): 1582 ν (C=N), 1511, 1442, 1394, 1259, 1014, 921, 776,755. TOF-MS-ES+ (*m*/*z*): calcd. For $[C_{20}H_{28}FeN_2O_4]^+$: 416.1398, found: 416.1409. Anal.: calcd. For $C_{20}H_{28}FeN_2O_4$ ·H₂O: C, 55.31; H, 6.96; N, 6.45; found: C, 55.79; H, 6.78; N, 6.29.

2.3.6 | 2-(2,4,4-trimethylpentan-2yliminomethyl)pyridyliron (II) acetylacetonate Fe6

Green solid, 152 mg, 41% yield. ATR-IR (cm⁻¹): 1582 ν (C=N), 1511, 1442, 1394, 1259, 1014, 921, 776,755. TOF-MS-ES+ (*m*/*z*): calcd. For [C₂₄H₃₆FeN₂O₄]⁺: 472.2024, found: 472.2022. Anal.: calcd. For C₂₄H₃₆FeN₂O₄·H₂O: C, 58.78; H, 7.81; N, 5.71; found: C, 57.95; H, 7.26; N, 5.63.

2.4 | Polymerization procedure

The polymerization of isoprene in toluene was carried out in a 25 ml Schlenk reactor. In a typical process, the reactor was dried in vacuum and refilled back with argon for more than three times. The iron complex was weighed in glove box and then added into a Schlenk reactor. The required amount of solvent, cocatalyst and isoprene was sequentially added into the reactor under argon atmosphere. After the required time of reaction, the polymerization quenched with HCl solution in methanol (methanol/HCl = 50/1). The resulting suspension was poured into a large volume of methanol containing 2,6bis(1,1-dimethylethyl)-4-methylphenol (BHT) as the stabilizing agent. The polymer was collected by filtration and washed with ethanol for several times and dried under vacuum at room temperature until no change was observed in weight. The polymer yields were determined by gravimetry.

3 | **RESULTS AND DISCUSSION**

3.1 | Synthesis and characterization of iron complexes (Fe1-Fe6)

A series of 2-(aryl/alkyliminomethyl)pyridyliron (II) acetylacetonate complexes: (aryl = Ph **Fe1**; alkyl = CH₂Ph **Fe2**, CH (Ph)₂ **Fe3**, CH (Me)₂ **Fe4**, C (Me)₃ **Fe5**, C (Me)₂CH₂C(Me)₃ **Fe6**), has been prepared in moderate yields (39–67%) by the treatment of Fe (acac)₂ with the corresponding 2-(aryl/alkyliminomethyl)pyridine ligands under argon atmosphere (Scheme 1). The ligands were prepared by two-step procedure reported elsewhere^[38] and characterized by ¹H/¹³C NMR spectroscopy. The identity and purity of complexes were determined by ATR-IR and mass spectroscopies, and elemental analysis. Additionally, the molecular structure of **Fe2** has been established by X-ray diffraction analysis.

X-ray quality crystals of complex **Fe2** was obtained by the slow evaporation of its dichloromethane solution under air at room temperature, indicating obtained crystals were air and moisture stable. The prospective view of molecular structure of **Fe2** is shown in Figure 1. The structure of **Fe2** is mononuclear species having hexacoordinate geometry best described as distorted octahedron: the N2_{imine}, O1_{acac}, O2_{acac} and O4_{acac} atoms form the basal square plane while N1_{pyridine} and O3_{acac} atoms occupy the apical position. The O3-Fe1-N1 angle [163.71(9)°] is modestly bend from the linear, it might be due to the ring strain induced by chelation of iminopyridine and acetylacetone anions with metal center. More distortions are observed in the O2-Fe1-N2 angle



SCHEME 1 Synthesis of 2-(aryl/alkyliminomethyl)pyridine ligands and their iron (II) acetylacetonate complexes



FIGURE 1 The molecular structure of complex Fe2

[158.95(8)°], however, O4-Fe1-O1 angle exhibited more linear features [176.49(8)°]. In addition, modest variations in the bite angles of acetylacetonate anion was observed as O1-Fe1-O2 is smaller than O3-Fe1-O4 angle of [83.74(8)° vs. 86.24(8)° respectively] can be ascribed to the steric hindrance induced by the bulky N-aryl group. In comparison with structurally related iron complexes bearing chloride auxiliary ligands instead of acetylacetonate reported by Ritter and his co-workers,^[38] some significant variations in the band angles and lengths were observed. For instance, the bite angle N1-Fe1-N2 $[74.57(9)^{\circ}]$ in **Fe2** is found to be smaller than that was observed in the iron (II) chloride analogue [78.3(2)°]. Similarly, the Fe-N_{imine} and Fe-N_{pyridine} bond distances [Fe1-N1 2.312(2) Å and Fe1-N2 2.224(2) Å respectively] are all longer than that have been reported for iron (II) chloride complex [Fe1-N2A 2.121(6) Å and Fe1-N1A 2.119(5) Å) respectively], possibly strong negative electronic effect of chloride as compared to the acetylacetonate is influential to induce these structural variations.

3.2 | Isoprene polymerization

In order to determine the catalytic potential of the iron (II) acetylacetonate (Fe1-Fe6) in isoprene polymerization, preliminary tests were performed using solely Fe2 with a range of different aluminumalkyl cocatalysts. including methylaluminoxane (MAO), triisobutylaluminum $(Al(i-Bu)_3)$ and triethylaluminum (AlEt₃). Typically, the tests were performed at 25 °C in toluene (5 mL) with the ratio [Fe]/[Ip]/[Al] of 1/2000/ 500 over different period of time to reach the maximum yield; the results of this initial screening are presented in Table 1. Examination of the data, reveals Fe2 is active with only MAO cocatalyst offering quantitative yield (>99%) over run time of 10 min, while with other two cocatalysts, was essentially inactive (Table 1, entries 2 & 3). On the basis of these findings, subsequent more in-depth studies focused on the use of MAO as the co-catalyst for the activation of all other complexes (Fe1, Fe3-Fe6). Worthy to mention that this is first example of iron (II) catalysts in which well-defined iminopyridine iron (II) acetylacetonate complex used for olefin polymerization.

With the intent to establish a correlation of structural variations in the pre-catalysts with their catalytic performance, all the iron complexes were employed for isoprene polymerization and the resulting polymerization data are collected in the Table 2 (Figure 2). Upon activation with MAO cocatalyst, the pre-catalysts (**Fe1–Fe6**) displayed good to excellent activities (Table 2, entries 1–6). On the other hand, Fe (acac)₂ was found to be essentially inactive toward the isoprene polymerization highlighting the key role of ligand in stabilizing the active species and thereby high activities (Table 2, entry 7). The overall catalytic activities of **Fe1–Fe6** decreased in the order: **Fe1** [Ph] ~ **Fe2** [CH₂Ph] ~ **Fe3** [CH (Ph)₂] ~ **Fe4** [CH (Me)₂] > **Fe5** [C (Me)₃] > **Fe6** [C (Me)₂CH₂C(Me)₃]. Though complexes **Fe1–Fe4** were

			Yield ^b	Act. ^c	$M_n^{\rm d}$	M _w/	Microstructure(%) ^e		
Entry	Cocat.	Time	(%)	(×10 ⁻⁵)	(×10 ⁻⁴)	$M_n^{\rm d}$	trans-1,4	<i>cis</i> -1,4	3,4
1	MAO	10 min	>99	8.2	6.7	2.2	10	36	54
2	Al(<i>i</i> -Bu) ₃	16 h	0	-	-	-	-	-	-
3	AlEt ₃	16 h	0	-	-	-	-	-	-

^aGeneral conditions: catalyst **Fe2**; [Ip] = 4.0 mol/L; [Fe]/[Ip]/[cocat.] = 1/2000/500; toluene (5 ml); reaction temperature 25 °C.

^bIsolated yield.

 $^{c}g_{Polymer}$ (mol of Fe)⁻¹ h⁻¹.

^dDetermined by gel permeation chromatography (GPC).

 $^{e}\mbox{Determined}$ by $^{1}\mbox{H}$ and $^{13}\mbox{C}$ NMR.

TABLE 2 Isoprene polymerization using Fe1-Fe6/MAO and Fe (acac)₂/MAO^a

			Yield ^b (%)	Act. ^c (×10 ⁻⁵)	${M_n}^{ m d}$ (×10 ⁻⁴)	$M_w/M_n^{ m d}$	Microstructure(%) ^e		
Entry	Cat.	Time					trans-1,4	cis-1,4	3,4
1	Fe1	10 min	>99	8.2	4.3	3.3	0	51	49
2	Fe2	10 min	>99	8.2	6.7	2.2	10	36	54
3	Fe3	10 min	>99	8.2	6.5	2.7	3	55	42
4	Fe4	10 min	>99	8.2	5.8	2.7	16	39	45
5	Fe5	2 h	>99	0.7	1.7	3.0	74	12	14
6	Fe6	2 h	55	0.4	1.2	2.0	87	3	10
7	Fe (acac) ₂	16 h	-	-	-	-	-	-	-

^aGeneral conditions: [Ip] = 4.0 mol/L; [Fe]/[Ip]/[MAO] = 1/2000/500; toluene (5 ml); reaction temperature 25 °C.

^bIsolated yield.

 $^{c}g_{Polymer} \text{ (mol of Fe)}^{-1} \text{ h}^{-1}.$

^dDetermined by gel permeation chromatography (GPC).

 $^{e}\mbox{Determined}$ by $^{1}\mbox{H}$ and $^{13}\mbox{C}$ NMR.



FIGURE 2 Activities and conversion of isoprene polymerization using different precatalysts (Table 2, entries 1–7)

the standout performers showing the highest activities (up to 8.2×10^5 g_{Polymer} (mol of Fe)⁻¹ h⁻¹). The precise explanation behind these differences in catalytic performance remain unclear but would be relate to the negative inductive effect of imino group increasing the stability of

the iron active species in favour of high activities. Meanwhile, it is also noted that the electronic effect through resonance also affect the molecular weights of resultant polymer: Fe2 [CH₂Ph] and Fe3 [CH (Ph)₂] based polymers exhibited the highest molecular weight (Table 2, entries 2 & 3). As can be seen in the GPC curves in Figure 3, molecular weight distributions are unimodal $(M_{\rm w}/M_{\rm n} = 2.0-3.3)$ suggesting single-site catalytic behavior of title iron complexes systems. The microstructures of the resultant polyisoprene were analyzed by ¹H/¹³C NMR spectroscopy and their ¹H NMR spectra can be seen in the Figure 4. In general, all complexes showed poor to good regio-selectivities. The Fe1-Fe4 based polyisoprene mainly composed of cis-1,4 and 3,4 units, particularly polymer obtained using Fe1 possessed nearly equal amount of cis-1,4 (51%) and 3,4 (49%) units. However, in case of Fe5 and Fe6 based polymer contained notable amount of trans-1,4 units (74% and 87% respectively) with small amount of cis-1,4 and 3,4 units (Table 2, entries 5 & 6). In comparison with structurally related



FIGURE 3 GPC curves of polyisoprene obtained using **Fe1-Fe6**/ MAO catalyst system (Table 2, entry 1–6)



FIGURE 4 ¹H NMR spectra of the polyisoprene obtained with **Fe1-Fe6** (Table 2, entries 1–6)

iron (II) chloride complexes bearing *N*-octamyl group reported by Chen *et al.*, **Fe6** showed slightly lower catalytic performance regarding activity, molecular weight and distribution.^[39] However, polyisoprene showed better *trans*-1,4 regio-selectivities (*trans*-1,4 units of 87% *vs. cis*-1,4 units of 77%). This would be due to the different activation process as title complexes contained acetylacetonate instead of chloride, stability of active species and different counter ion.

In comparison with previously reported related iron, herein reported catalysts showed a better catalytic performance in term of activities. For instance, the precatalysts bearing very similar ligand support to the previously precatalysts reported by our group showed lower activates as required 2 h reaction time for complete conversions,^[40] while iron catalysts reported herein only required 1 min for 100% conversion (Table S1, entries 1–4). Similar results were found when compared the activities with catalysts reported by the groups of Ritter^[38] and Chen.^[39] It can be assumed that titled catalysts bearing acetylacetonate instead of halide would have impact on the activation process and stability of active species; therefore higher activities were achieved. Concerning microstructural properties, comparatively poor regio-selectivity of monomer enchainment was obtained with the titled pre-catalysts. Meanwhile, the catalytic activities of pre-catalysts (**Fe1–Fe4**) are substantially higher than reported cobalt halide analogues.^[9,39,40]

Further polymerization tests were performed using the Fe2 and Fe6 to examine the effect of different amount of cocatalyst and reaction temperature. The resulting polymerization data is collected in the Table 3. Changes in the amount of cocatalyst showed moderate effect on the catalytic activities and properties of the resulting polymer. When Al/Fe2 ratio was decreased from 500 (Table 2, entry 2) through 100 to 50 and temperature kept at 25 °C, catalytic activities remained unchanged (Table 3, entries 1-2). On further decreasing the Al/Fe ratio to 10, the activity slightly decreased to $8.0 \times 10^5 g_{Polymer}$ (mol of $Fe)^{-1}h^{-1}$ (Table 3, entry 3), but still it maintained high activity even on small amount of cocatalyst loadings. However, no polymer at all was obtained with Al/Fe ratio of 5 (Table 3, entry 4). The number molecular weight consistently increased with decrease of cocatalyst loading, but reached to a lower value of 1.1×10^5 g/mol at an Al/Fe ratio of 50 (Table 3, entry 2). On further decreasing of Al/Fe ratio, number molecular weight again increased to 2.0×10^5 g/mol (Table 3, entry 3) and the variations in number molecular weight might be due to the mass transport problems as the catalyst becomes increasingly embedded in the polymer. In the similar way, negligible influence of variations in the cocatalyst loadings on the molecular weight distributions and regio-selectivities of the resultant polymer was observed. With the fixed Al/Fe ratio at 50, thermal stability of Fe2/MAO was examined by performing polymerization tests at different temperatures namely -30 and 50 °C (Table 3, entries 5 & 6). Interestingly, catalytic activities remained high (activity: 8.2 \times 10⁵ g_{Polymer} (mol of Fe)⁻¹ h⁻¹) as was observed at 25 °C indicating high thermal stability of active species either polymerization perform at very low temperature of -30 °C or at high temperature of 50 °C. The molecular weight of polyisoprene was reduced from 11.5×10^5 g mol⁻¹ to 8.6×10^5 g mol⁻¹ on raising the reaction temperature from 25 °C to 50 °C. It would be due to the high rate of chain transfer reaction at elevated temperature. For the obtained polyisoprene, cis-1,4-/3,4units with ratio of 1/1 was the major part of the resultant polyisoprene when the reaction temperature decreased to 8 of 10 WILEY Organometalli Chemistry

TABLE 3 Isoprene Polymerization under different reaction conditions^a

		[Fe]/ [MAO]	Time (min)	Yield ^b (%)	Act. ^c (×10 ⁻⁵)	<i>M</i> _n ^d (×10 ⁻⁴)	$M_w/$	Microstructure(%) ^e		
Entry	Cat.						M_n^{d}	trans-1,4	<i>cis</i> -1,4	3,4
1	Fe2	1/100	10	>99	8.2	12.8	1.7	9	37	54
2	Fe2	1/50	10	>99	8.2	11.5	1.9	9	39	52
3	Fe2	1/10	10	98.5	8.0	19.6	1.8	6	41	53
4	Fe2	1/5	10	0						
$5^{\rm f}$	Fe2	1/50	10	>99	8.2	10.7	2.3	0	45	55
6 ^g	Fe2	1/50	10	>99	8.2	8.6	2.1	13	38	49
7 ^h	Fe2	1/50	10	85	69.3	11.9	1.8	9	38	53
8^{f}	Fe6	1/500	120	2.5	0.02	0.6	1.4	36	32	32
9 ^g	Fe6	1/500	120	19.8	0.1	0.7	1.9	80	7	13
10	Fe6	1/500	180	75	0.3	1.5	1.9	86	4	10
11	Fe6	1/500	300	92	0.3	1.9	1.7	86	5	9

^aGeneral conditions: [Fe]/[Ip] = 1/2000, [Ip] = 4.0 mol/L; toluene (5 ml), 25 °C.

^bIsolated yield.

 $^{c}g_{Polymer} \text{ (mol of Fe)}^{-1} \text{ h}^{-1}.$

^dDetermined by gel permeation chromatography (GPC).

^eDetermined by ¹H and ¹³C NMR.

^f30 °C.

^g50 °C.

 h [Fe]/[Ip] = 1/20000, [Ip] = 4.0 mol/L; toluene (50 ml), 25 °C.

-30 °C. These finding suggesting that higher temperature favour *trans*-1,4 selectivity which can be switched to *cis*-1,4/3,4 selectivity by decreasing the reaction temperature. Meanwhile, when the catalyst loading of **Fe2** was decreased to 0.005%, catalytic activities substantially improved from 8.2 × 10⁵ to 69.3 × 10⁵ g_{Polymer} (mol of Fe)⁻¹ h⁻¹.

Considering the high selectivities obtained by Fe6, the influence of reaction temperature and time on the catalytic performance of this catalyst was additionally studied (Table 3, entries 8 & 9). The change in temperature showed a negative effect on the catalytic activities as well as the properties of the resultant polymer (Table 3, entry 8 & 9). At -30 °C, the selectivity of *trans*-1,4 units significantly reduced from 87% (25 °C) to 36% (Table 3, entry 8). Similarly, this selectivity slightly reduced to 80%, when polymerization performed at 50 °C (Table 3, entry 9). On prolonging the reaction time to 3 h and 5 h while other conditions including Al/Fe ratio and temperature fixed at 500 and 25 °C, monomer conversion gradually improved to 92% over run time of 5 h highlighting longer lifetime of the active species. Meanwhile, no effect of reaction time was observed on the properties of the obtained polymer (Figure 5).

Bearing in mind the microstructural properties of the obtained polyisoprene, we proposed a general mechanism



FIGURE 5 Variation in conversions of isoprene and *trans*-1,4 units of polymer over different run times (Table 2, entry 6 & Table 3, entries 10 & 11)

for these iron catalyzed isoprene polymerization as given in the Scheme S1 (see Supporting information). The polymer obtained by title iron catalysts being different from the previously reported iron chloride catalyzed isoprene polymerization,^[39] indicates a different activation process thus lead to different counterions. Upon activation with MAO, a heterobimetallic intermediate I or II (Scheme S1) would form during the activation process: two metals centers (Fe and Al species) connected through acetylacetone in which one oxygen atom of acetylacetone coordinated to iron center and remaining oxygen atom bonded to aluminum center.^[10] The type of monomer insertion and subsequent monomer enchainment are the key steps that determine the end structural properties of the polymer. Following the initial coordination of monomer at vacant site of iron center either through *cis*- η^4 or *trans*- η^4 coordination (**III** and **IV** in Scheme S1) and insertion of coordinated monomer to Fe-alkyl bond leading to the formation of anti- η^3 or syn- η^3 allyl-Fe intermediates (V and VI in Scheme S1) respectively, and then multiple coordination-insertion steps proceed leading to chain growth (propagation step). In the case of multiple $cis-\eta^4$ type coordination-insertion (VII), the produced polyisoprene would be expected to be cis-1,4-unit if no isomerization of syn- η^3 allyl type of chain end occurs. If multiple coordination-insertion of isoprene was happened as in VIII (Scheme S1), then trans-1,4 enriched polymer is likely; if as is in IX or/and X (Scheme S1), then 3,4-polyisoprene is likely to achieve. In the case of **Fe6** mediated polymerization, *trans*- η^4 type of coordination-insertion of monomer would be expected to be involved as trans-1,4 unit enriched polyisoprene was obtained. While, for sterically less hindered complexes (such as Fe1-Fe4) based polymerization, both $cis-n^4$ and $cis-n^2$ or trans- n^2 type of monomer coordination-insertion is likely to be involved in the propagation step. Similar findings have been found in the literature.^[47–50]

4 | CONCLUSION

In summary, a series of well-defined ferrous acetylacetonate complexes bearing iminopyridine ligand were synthesized and fully characterized by ATR-IR and mass spectroscopies, and elemental analysis; single crystal X-ray diffraction in the case of Fe2. All complexes were tested for the polymerization of isoprene in combination with MAO, and found that reaction conditions and type of ligand have influences on both activity and stereoselectivity. The complexes (Fe1-Fe6) displayed high activities as high as 7×10^6 g·(mol of Fe)⁻¹·h⁻¹. Meanwhile, sterically less crowded Fe6 gave polyisoprene with higher trans-1,4-unit content (up to 87%). Compared to the reported ferrous chloride complex, the title ferrous acetylacetonate complexes exhibited substantially different catalytic behavior for isoprene polymerization indicating the key role of counteranion in the monomer insertion and chain propagation. Further exploration of isoprene polymerization mechanism is currently in progress in our laboratories.

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SUPPORTING INFORMATION

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