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Highly *trans*-1,4 selective polymerization of 1,3-butadiene initiated by iron(III) bis(imino)pyridyl complexes

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ABSTRACT

A series of 2,6-bis(imino)pyridyl iron(III) complexes of the general formula $[2,6\text{-}(ArN{=}CMe)_2C_5H_3N]FeCl_3$ (Ar = $-C_6H_5$, **3a**; 2-MeC_6H_4, **3b**; 2-EtC_6H_4, **3c**; 2-$^iPrC_6H_4$, **3d**; cyclohexyl, **3e**; 4-MeC_6H_4, **3f**; 4-$^iPrC_6H_4$, **3g**; 4-FC_6H_4, **3h** and 4-$CF_3C_6H_4$, **3i**), activated by alkylaluminum, MAO or MMAO, have been investigated in 1,3-butadiene polymerization. Iron(III) complex (**3a**), with the least steric hindrance around the metal center, gives polymer up to 99% in yield in 4 h (butadiene to iron ratio = 1000), and *trans*-1,4 selectivity about 94.7% at room temperature in toluene, while those (**3b**–**3d**) bearing alkyl substituents at the 2-position of each *N*-aryl ring exhibit much lower catalytic activity and tunable *trans*-1,4 selectivity. Introduction of an alkyl group at the 4-position (*para*-position, **3f** and **3g**) exerts a slightly beneficial effect on the *trans*-1,4 selectivity, while electronegative groups at the same position (**3h** and **3i**) affect negatively on the activity. The effects of temperature, types of cocatalyst and Al/Fe molar ratio on the polymerization behavior are investigated. More importantly, a mechanism for forming *trans*-1,4 structure is also proposed.

1. Introduction

The development of well-defined transition metal catalysts for highly regio- and/or stereoselective polymerization of butadiene has attracted considerable attention in polydienes areas [1–15], because the resultant polymers find wide applications in gloves, tube, tire industry, etc. Among the transition metals, high active and selective iron-based catalysts featured an expedient preparation, low toxicity and high tolerance to moisture and air are highly anticipated. However, low activity, poor selectivity and extremely low molecular weight of resultant product are generally the tough issues in iron-based catalysts. In spite of these, there has been a considerable and growing interest in designing and synthesizing ancillary electron donor or ligand to improve catalytic performance over the past decade, and partial success has been achieved in some systems. The activity has been improved by introducing bidentate ligands such as 1,10-phenanthroline or 2,2′-bipyridine into iron dichloride complexes, but the formed catalysts only gives equivalent *cis*-1,4 and 1,2-polybutadiene at room temperature, high selectivity (1,2-selectivity: 91%) can be available only at −78 °C at the expense of activity [16,17]. To date, progresses have been made since dialkylphosphite and phosphate are invented as an important component in the iron-based catalyst in our group and by Luo, with which syndiotactically enriched 1,2-polybutadiene (1,2-: 87–95%, pentad *rrrr*: 65–95%) can be obtained in butadiene polymerization [18–24], albeit by a poorly structurally defined catalyst and an unclear mechanism of formation of the active site. In comparison with the versatile cobalt- and vanadium-based catalysts, research on the iron counterparts has been relatively limited. Until recently, a few on with high 1,4-selectivity and some with 1,2-selectivity have started to emerge [25–29]. Therefore, organometallic iron-based catalysts with well-designed structure for high 1,4-selective polymerization of butadiene are quite challenging and highly desired.

Over the past decade, the field of olefin polymerization catalysts has undergone an important renewal with the discovery of extremely high active iron(II) and cobalt(II)chloride carrying 2,6-bis(imino)pyridyl ligands [30–33]. Encouraged by this initiation, *N*,*N*,*N*-type auxiliary ligands have received an upsurge in research interest and numerous corresponding metal complexes have emerged in the olefin field [34–40]. The impressive activity of late transition metal complexes bearing 2,6-bis(imino)pyridyl ligands, especially, more remarkable activity of iron derivatives, in ethylene polymerization indicates the significance of such kind of ligands in olefin polymerization, presumably, the finding that may be relevant for the diene polymerization area. Study on iron-complex bearing such ligands for butadiene polymerization, seems to be

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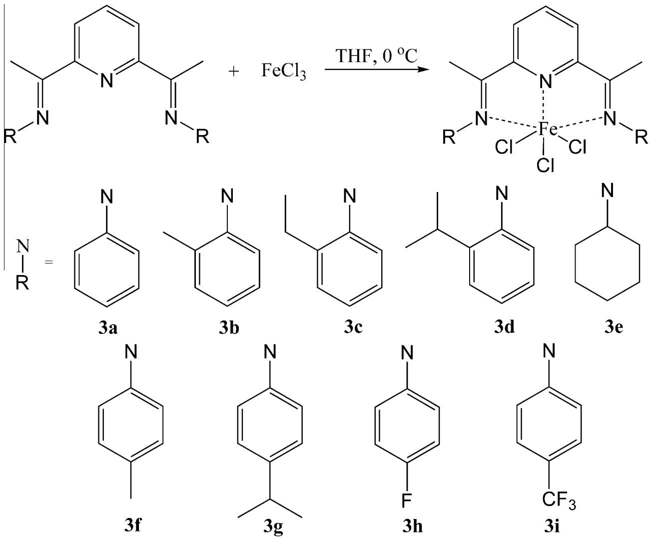


Scheme 1. The structures of complexes (**3a**–**3i**).

quite limited [25,29,41,42]. Although the additional neutral donors, such as dialkylphosphite and phosphate, as demonstrated previously, can also act as effecitve ligands in occupying unsaturated coordination site of metal center as a potential shelter for deactivating poison, as well as in stiffening the structure of the complex, thus, facilitating regio- and/or stereoselective polymerization, the latter (*N*,*N*,*N*-ligand) is more attractive due to more constrained environment and more tunable features endowed with such tridentate framework, which may deliver a clear image on the relationship between steric and electronic characteristics of substituents and polymerization behaviors, especially, the stereoselectivity.

We are interested in the 2,6-bis(imino)pyridyl ligand from two aspects essential for selective polymerization, i.e. stabilizing the central metal by the large electron conjugated system and inducing specific selectivity by constraining the central metal through the rigidness of ligand framework. Here, iron(III) complexes with steric and electronic modified 2,6-bis(imino)pyridyl ligands (Scheme 1), a new type of precursor, are synthesised for butadiene polymerization in the presence of cocatalysts. The facile modification of the ligand by varying the substituent on the iminoaryl ring, allows us to control the steric and electronic effects on the iron center, ultimately, paves the way to access the desired catalysts.

2. Experimental

2.1. General considerations

All manipulations for air- or/and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Anhydrous FeCl$_3$ and all anilines were purchased from Alfa Aesar. 2,6-Diacetylpyridine was purchased from Aldrich. Triisobutylaluminum (Al^{i}Bu$_3$), triethylaluminum (AlEt$_3$), methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) were commercially products from AkzoNoble. Toluene and tetrahydrofuran (THF) were freshly distilled in the presence of sodium and benzophenone. Polymerization grade butadiene was supplied from Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å molecular sieves and KOH. Other chemicals were used as received unless otherwise noted. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Varian Unity spectrometer in CDCl$_3$ at room temperature. IR spectra were performed on BRUKE Vertex-70 FIR spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. The proportion of 1,2, *cis*-1,4 and *trans*-1,4 units of polymer was determined by IR spectra, ^{1}H NMR and ^{13}C NMR [43,44]. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymer were measured at 30 °C by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF) and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weight of polymer was determined using the polystyrene calibration. DSC measurements were performed on a Perkin–Elmer Diamond differential scanning calorimeter at a heating rate of 10 °C/min.

2.2. Syntheses and characterizations of ligands (***2a***–***2i***) and complexes (***3a***–***3i***)

2.2.1. Syntheses and characterizations of ligands (***2a***–***2i***)

The ligands **2a**–**2i** were prepared by condensation reaction of excess appropriate anilines or amine with of 2,6-diacetylpyridine according to the literatures [33,37].

2.2.2. Preparation of complexes (***3a***–***3i***)

The complexes **3a**–**3i** were synthesised by reaction of FeCl$_3$ with the corresponding ligands in THF. A typical synthetic procedure for complex **3a** can be described as follows. Anhydrous iron(III) chloride powder (0.16 g, 1.0 mmol) and 2,6-bis[1-(phenylimino)ethyl]pyridine (0.31 g, 1.0 mmol) were added into an oxygen and moisture free flask containing cold THF (8 mL), then cooled to 0 °C for minimizing the undesired reduction of iron(III) to iron(II). The red precipitate (0.46 g, 97.9%) was collected after stirring for 1 h, followed by filtering, washing with heptane (3 × 5 mL) and drying in vacuum.

*2.2.2.1. {2,6-Bis-[1-(phenylimino)ethyl]pyridine}FeCl$_3$ (**3a**).* Yield: 97.9%. IR(KBr, cm^{-1}): 3079, 1626($\nu_{C=N}$), 1586, 1486, 1372, 1266, 1229, 1027, 777, 694. *Anal.* Calc. for $C_{21}H_{19}N_3FeCl_3$: C, 53.03; H, 4.03; N, 8.84.Found: C, 53.30; H, 3.89; N, 8.68%.

*2.2.2.2. {2,6-Bis-[1-(2-methylphenylimino)ethyl]pyridine}FeCl$_3$ (**3b**).* Yield: 92.8%. IR (KBr, cm^{-1}): 3058, 1622 ($\nu_{C=N}$), 1586, 1486, 1451, 1372, 1268, 1031, 755. *Anal.* Calc. for $C_{23}H_{23}N_3FeCl_3$: C, 54.85; H, 4.61; N, 8.34. Found: C, 54.50; H, 4.50; N, 8.68%.

*2.2.2.3. {2,6-Bis-[1-(2-ethylphenylimino)ethyl]pyridine}FeCl$_3$ (**3c**).* Yield: 85.4%. IR (KBr, cm^{-1}): 2972, 2875, 1623 ($\nu_{C=N}$), 1484, 1457, 1373, 1265, 1032, 748. *Anal.* Calc. for $C_{25}H_{27}N_3FeCl_3$: C, 56.47; H, 5.12; N, 7.90. Found: C, 56.80; H, 5.00; N, 7.68%.

*2.2.2.4. {2,6-Bis-[1-(2-isopropylphenylimino)ethyl]pyridine}FeCl$_3$ (**3d**).* Yield: 84.6%. IR (KBr, cm^{-1}): 2964, 2867, 1623 ($\nu_{C=N}$), 1585, 1485, 1444, 1372, 1266, 1030, 756. *Anal.* Calc. for $C_{27}H_{31}N_3FeCl_3$: C, 57.93; H, 5.58; N, 7.51. Found: C, 57.60; H, 5.70; N, 7.88%.

*2.2.2.5. {2,6-Bis-[1-cyclohexylimino)ethyl]pyridine)}FeCl$_3$ (**3e**).* Yield: 77.5%. IR (KBr, cm^{-1}): 2963, 2868, 1621 ($\nu_{C=N}$), 1584, 1485, 1444, 1368, 1267, 1209, 785. *Anal.* Calc. for $C_{21}H_{31}N_3FeCl_3$: C, 51.72; H, 6.41; N, 8.62. Found: C, 51.50; H, 6.60; N, 8.78%.

*2.2.2.6. {2,6-Bis[1-(4-methylphenylimino)ethyl]pyridine}FeCl$_3$ (**3f**).* Yield: 87.5%. IR (KBr, cm^{-1}): 2921, 1620 ($\nu_{C=N}$), 1584, 1505, 1372, 1267, 1232, 1028, 850, 817. *Anal.* Calc. for $C_{23}H_{23}N_3FeCl_3$: C, 54.85; H, 4.60; N, 8.34. Found: C, 54.99; H, 4.79; N, 8.15%.

*2.2.2.7. {2,6-Bis[1-(4-isopropylphenylimino)ethyl]pyridine}FeCl$_3$. (**3g**).* Yield: 90.5%. IR (KBr, cm^{-1}): 2960, 1624 ($\nu_{C=N}$), 1585, 1558, 1372, 1266, 1116, 857, 814. *Anal.* Calc. for $C_{27}H_{31}N_3FeCl_3$: C, 57.93; H, 5.58; N, 7.51. Found: C, 57.64; H, 5.64; N, 7.79%.

*2.2.2.8. {2,6-Bis[1-(4-fluorophenylimino)ethyl]pyridine}FeCl$_3$ (**3h**).* Yield: 65.5%. IR (KBr, cm^{-1}): 1623 ($\nu_{C=N}$), 1588, 1501, 1373, 1267, 1155, 1096,1029, 759, 817. *Anal.* Calc. for $C_{21}H_{17}F_2N_3FeCl_3$: C, 49.30; H, 3.35; N, 8.21. Found: C, 49.04; H, 3.59; N, 8.09%.

*2.2.2.9. {2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine}FeCl$_3$ (**3i**).* Yield: 58.5%. IR (KBr, cm^{-1}): 3011, 1611 ($\nu_{C=N}$), 1587, 1376, 1322, 1267, 1235, 1166, 1066, 871, 831, 668. *Anal.* Calc. for $C_{23}H_{17}F_6N_3FeCl_3$: C, 45.17; H, 2.80; N, 6.87. Found: C, 45.54; H, 2.70; N, 6.64%.

2.3. X-ray structure determinations

Data collections were performed at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data and collection parameters as well as the selected bond distances and angles are collected in Tables 1 and 2, respectively.

2.4. Procedure for butadiene polymerization

A typical procedure for the polymerization is as follows (entry 1 in Table 3): a toluene solution of butadiene (5 mL, 2.0 mol/L) was added to a moisture free ampoule bottle preloaded with complex **3a** (4.7 mg, 0.01 mmol). Al*i*Bu$_3$ (0.4 mL, 1.0 mol/L) was injected to initiate the polymerization at 20 °C. After 4 h, methanol was added

Table 2
Selected bond distances (Å) and angles (°) of complexes **3a**, **3d** and **3f**.

	3a	**3d**	**3f**
Fe–N1	2.118(5)	2.119(4)	2.1163(19)
Fe–N2	2.155(5)	2.177(3)	2.1794(19)
Fe–N3	2.151(5)	2.185(4)	2.178(2)
Fe–Cl1	2.2427(19)	2.2517(13)	2.2354(7)
Fe–Cl2	2.361(2)	2.3164(14)	2.3622(7)
Fe–Cl3	2.321(2)	2.3789(13)	2.3323(7)
N1–Fe–N3	72.9(2)	73.18(14)	73.33(7)
N1–Fe–N2	73.5(2)	73.74(14)	73.56(7)
N3–Fe–N2	146.13(19)	146.72(14)	146.86(7)
N1–Fe–Cl1	176.00(16)	175.90(11)	177.61(6)
N3–Fe–Cl1	109.37(14)	105.48(11)	104.58(6)
N2–Fe–Cl1	104.42(14)	107.77(10)	108.56(6)
N1–Fe–Cl3	87.57(14)	83.21(11)	86.25(5)
N3–Fe–Cl3	86.74(14)	90.70(12)	89.44(5)
N2–Fe–Cl3	87.62(14)	88.91(10)	87.11(6)
Cl1–Fe–Cl3	95.81(7)	92.97(5)	94.92(3)
N3–Fe–Cl2	89.13(15)	86.01(12)	90.16(5)
N2–Fe–Cl2	91.41(15)	89.83(11)	88.67(5)
N1–Fe–Cl2	83.63(14)	88.82(11)	85.65(5)
Cl1–Fe–Cl2	93.05(7)	94.97(5)	93.25(3)
Cl3–Fe–Cl2	171.05(7)	171.97(5)	171.66(3)

Table 3
Influence of substituents of iminoary moieties of complex on polymerization of butadiene.

Entry[a]	Complex	Yield (%)	M_n ($\times10^{-4}$)	M_w/M_n	Microstructure (%)			T_m[b]
					Trans-1,4	*Cis*-1,4	1,2	
1	**3a**	99	2.9	2.0	94.7	0	5.3	101
2	**3b**	25	25.3	2.9	43.2	13.6	43.2	–
3	**3c**	8	29.5	2.6	30.0	29.6	40.4	–
4	**3d**	10	27.8	2.7	10.0	43.6	46.4	–
5	**3e**	5	23.6	2.7	8.3	27.6	64.1	–
6	**3f**	99	3.7	2.2	95.1	0.2	4.7	109
7	**3g**	97	3.1	2.0	96.8	0.1	3.1	111
8	**3h**	64	3.0	2.1	93.4	0.4	6.2	98
9	**3i**	43	3.3	2.0	92.7	0.6	6.7	99

[a] Polymerization conditions: complex, 0.01 mmol; Al*i*Bu$_3$, 0.4 mmol; butadiene, 0.01 mol; toluene, 5 mL; temperature, 20 °C; time, 4 h.

[b] Melting temperature, determined by DSC.

Table 1
Crystal data and data collection parameters.

	3a·0.5C_6H_6	**3d**·2CH_2Cl_2	**3f**·0.5C_6H_6
Formula	$C_{21}H_{19}Cl_3N_3Fe\cdot0.5C_6H_6$	$C_{27}H_{31}Cl_3N_3Fe\cdot2CH_2Cl_2$	$C_{23}H_{23}Cl_3N_3Fe\cdot0.5C_6H_6$
Molecular weight	514.65	729.60	542.70
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/n
a (Å)	13.369(3)	15.9012(10)	12.2348(5)
b (Å)	9.5751(19)	12.5736(8)	14.8542(6)
c (Å)	19.502(4)	18.4593(11)	14.2180(6)
α (°)	90	90	90
β (°)	103.652(4)	112.4350(10)	91.3540(10)
γ (°)	90	90	90
V (Å^3)	2425.9(8)	3411.3(4)	2583.23(18)
Z	4	4	4
D_{calc} (Mg/m^3)	1.409	1.421	1.395
Absorption coefficient (mm^{-1})	0.968	1.014	0.913
F(0 0 0)	1056	1500	1120
Crystal size (mm)	0.12 × 0.09 × 0.06	0.38 × 0.09 × 0.08	0.22 × 0.19 × 0.08
θ Range (°)	1.57–25.07	2.01–25.36	1.98–26.07
Noumber of reflections collected	12 330	17 705	14 145
Number of independent reflections (R_{int})	4278 (0.1308)	6228 (0.0938)	5108 (0.024)
Number of data/restraints/parameters	4278/3/282	6228/0/367	5108/0/302
Goodness-of-fit (GOF) on F^2	0.963	1.061	1.051
R_1 (I > 2sigma(I))	0.0742	0.0691	0.0371
wR_2	0.1125	0.1685	0.9988

to the system to quench the polymerization. The mixture was poured into a large quantity of methanol containing 2,6-di-*tert*-butyl-4-methylphenol (1.0 wt.%) as a stabilizer. After filtration and drying under vacuum at 40 °C to constant weight, polybutadiene was collected (0.53 g, 99%).

3. Results and discussion

3.1. Syntheses and characterization of ligands and complexes

2,6-Bis(iminoethyl)pyridine derivatives (**2a**–**2i**) are readily prepared by condensation of anilines with 2,6-diacetylpyridine in CH_2Cl_2 in the presence of a calculated amount of acid. Complexes (**3a**–**3i**) are synthesised by reaction of anhydrous iron(III) chloride with the corresponding ligands in THF. All complexes are characterized by the elemental analyses and IR spectra. The elemental analyses results reveal that the components of all complexes are in accord with the formula $FeCl_3L$. The IR spectra of the free ligands show that the C=N stretching frequencies appear at 1648–1633 cm^{-1}, which shift toward lower frequencies to 1626–1611 cm^{-1} in the complexes together with greatly reduced intensity, indicating the coordination interaction between the imino nitrogen atoms and the metal ions occurs. Complexes **3a**, **3d** and **3f** are further characterized by X-ray crystallography and the crystal structures of **3f** is depicted in Fig. 1.

The conformers of the complexes **3a**, **3d** and **3f** are isomorphous, all having approximate *Cs* symmetry about a plane formed by the iron atom, the three chlorine groups and the pyridyl nitrogen atom. The geometry around the iron atom could be described as a distorted octahedron with the equatorial plane formed by three nitrogen atoms, one chlorine ligand (Cl(1))and the two axial Fe–Cl bonds. The deviations of the metal ion from the plane formed by the coordinated nitrogen atoms in **3a**, **3d** and **3f** are 0.1127, 0.0940 and 0.0338 Å, respectively. Three chlorine ligands are in a meridional geometry. The Fe–Cl bond distances located at *trans* position (Fe–Cl(1)) to pyridine are shorter than those at *cis* position to pyridine (Fe–Cl(2)) in three complexes. The Fe–Cl(2) bond distance in **3d** is shorter than the corresponding distances in **3a** and **3f**, while Fe–Cl(3) bond in **3d** is longer than its analogs. The Fe–N(pyridyl) bond distances of complexes are about 0.035–0.070 Å shorter than that of Fe–N(imino), and Fe–N(imino) bonds in **3a** are about 0.03 Å shorter than the counterparts in **3d** and **3f**. The planes of the phenyl rings are all oriented essentially orthogonal to the coordination planes of the bis(imino)pyridine unit. The two imino C=N bonds have typical double bond character with C=N bond lengths from 1.277(7) to 1.291(3) Å.

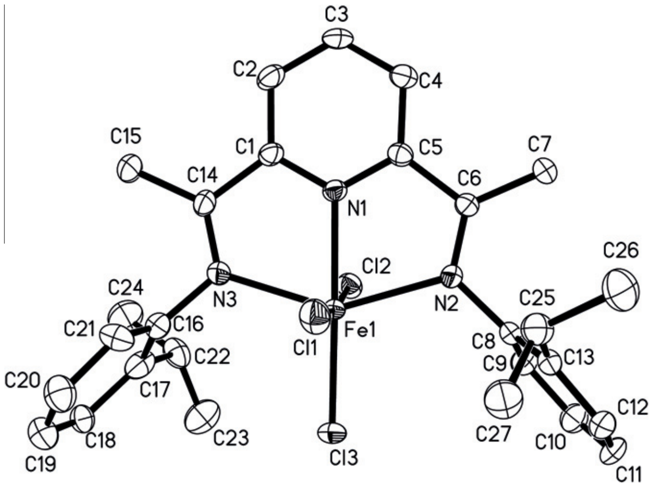


Fig. 1. ORTEP view of the complex **3f**, drawn at 35% of probability. Hydrogen atoms and the benzene molecule were omitted for clarity.

Table 4
Effects of temperature on polymerization of butadiene with complex **3a**.

Entry[a]	Temp (°C)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)			T_m[b]
					Trans-1,4	*Cis*-1,4	1,2	
10	−20	13	1.7	1.4	84.7	2.3	13.0	90
11	0	93	2.3	2.3	85.0	2.6	12.4	82
12	20	99	2.9	2.0	94.7	0	5.3	101
13	40	78	2.6	1.9	94.5	0	5.5	100
14	60	40	2.5	1.8	93.5	0	6.5	97

[a] Polymerization conditions: complex **3a**, 0.01 mmol; $\mathrm{Al^iBu_3}$, 0.4 mmol; butadiene, 0.01 mol; toluene, 5 mL; time, 4 h.
[b] Melting temperature, determined by DSC.

Table 5
Effects of Al/Fe molar ratio and type of Al on polymerization of butadiene with complex **3a**.

Entry[a]	Type of Al	Al/Fe (equiv)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)			T_m[b]
						Trans-1,4	*Cis*-1,4	1,2	
15	$\mathrm{Al^iBu_3}$	20	98	2.8	2.1	94.7	0	5.3	103
16	$\mathrm{Al^iBu_3}$	40	99	2.9	2.0	94.7	0	5.3	101
17	$\mathrm{Al^iBu_3}$	80	99	2.7	1.9	94.6	0	5.4	103
18	$\mathrm{Al^iBu_3}$	150	97	2.8	1.9	94.7	0	5.3	98
19	MAO	50	100	2.9	2.0	94.8	0	5.2	101
20	MAO	100	100	2.7	1.9	94.0	0	6.0	103
21	MMAO	50	99	3.1	1.8	95.4	0	4.6	98
22	MMAO	100	99	2.9	2.0	94.1	0	5.9	99
23	$\mathrm{AlEt_3}$	20	90	1.4	1.3	95.5	0	4.5	100
24	$\mathrm{AlEt_3}$	40	92	1.0	1.9	94.9	0	5.1	97

[a] Polymerization conditions: complex **3a**, 0.01 mmol; butadiene, 0.01 mol; toluene, 5 mL; temperature, 20 °C; time, 4 h.
[b] Melting temperature, determined by DSC.

3.2. Butadienepolymerization behaviors

As reflected in Tables 3–5, the catalytic productivity, microstructure and molecular weight of polymer are significantly affected by the nature of the substituent on the ligand frame, consistent with the cases of ethylene polymerization and oligomerization with transition metals bearing such kind of ligands [33]. In the meanwhile, catalytic performances are less affected by the variation of polymerization conditions, such as Al/Fe molar ratio, types of cocatalyst and polymerization temperature.

3.2.1. Substituent at the ortho-position

Iron(III) complex **3a**, possessing the least steric hindrance around the iron atom among all the complexes is the most active one, polymerizing butadiene in nearly 100% yield. The obtained polybutadiene possesses 94.6% *trans*-1,4 chain structure (Fig. 2) with molecular weight of 2.9×10^4 g/mol and molecular weight distribution (M_w/M_n) about 2.0, indicating polymerizations are probably performed by a single active site. Interestingly, incorporation of sterically bulky alkyl groups onto the 2-positions of each *N*-aryl moiety remarkably influences the polymerization behaviors. With the group at 2-position of each phenyl ring of the ligand in complexes gradually varying from 2-H (**3a**), 2-methyl (**3b**), 2-ethyl (**3c**) to 2-isopropyl (**3d**), both the yield and *trans*-1,4 selectivity decrease, from 99% to 10% in the yield and 94.6% to 10% in the *trans*-1,4 selectivity, while the molecular weight of yielded polymer jumps from 2.9×10^4 g/mol (**3a**) to 25.3×10^4 g/mol (**3b**), and then

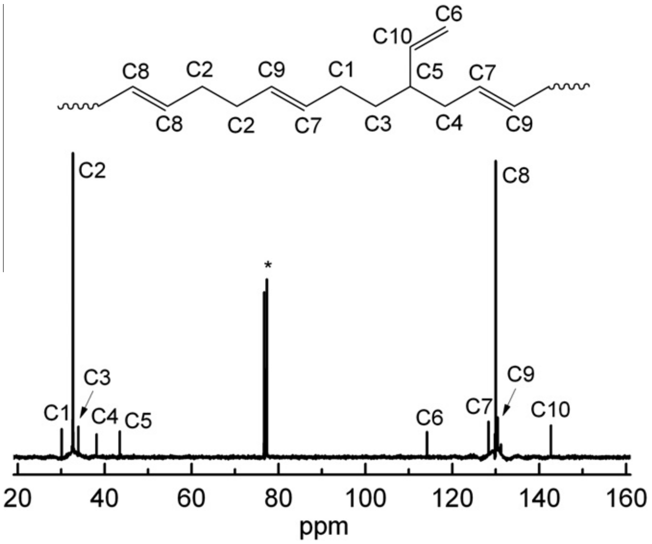


Fig. 2. The ^{13}C NMR of *trans*-1,4 polybutadiene (entry 1 in Table 3).

becomes insensitive to the size of the group at the 2-position. The decreased catalytic activity can possibly be ascribed to increased difficulty for coordination of butadiene monomer to the iron center, as the space around the metal center becomes more crowded [45] and the substantial increased molecular weight of polymer can probably be attributed to the suppressed β-hydride elimination and favoring chain propagation rate over chain transfer rate. Similar results have been shown in ethylene oligomerization and polymerization using catalysts bearing 2,6-bis[(iminoaryl)ethyl]pyridine ligand with the bulky group at the *ortho*-positions of the *N*-arylgroups [33,46,47]. Surprisingly, *trans*-1,4 selectivity decreases with the increment of the bulkiness of the group at the 2-positions though the correlation need to be explained further.

Interestingly, replacement of the phenyl group in **3a** with cyclohexyl, a nonconjugated substituent, in both *N*-aryl moieties of the ligand (**3e**) also witnesses a substantial decay in the activity and a remarkable decline in *trans*-1,4selectivity. The results may imply that the large and rigid π-system is essential in maintaining both the catalytic activity and high *trans*-1,4 selectivity. On one hand, the large π-system of ligand system exerting as an electroning withdraw moiety, increases the Lewis-acidity of the metal center, thus, facilitates coordination of butadiene monomer and impacts positively on the polymerization activity, on the other hand, the cyclohexyl group is more flexible compared to the phenyl group, and such flexibility may go against the *trans*-1,4 selectivity.

3.2.2. Substituent at the 4-position

The effects of 4-substituents on the iminophenyl rings on polymerization behavior were also evaluated while leaving the 2-positions on each iminoary ring open. As seen from entries 5 and 6 in Table 3, complexes **3f** and **3g** with methyl and isopropyl group at the4-positions, respectively, show marginally higher *trans*-1,4 selectivity (95.1% and 96.8%, respectively) than the benchmark complex **3a**, while the activity is maintained as high as its analog **3a**. Interestingly, while the high *trans*-1,4 selectivity is kept, the yield decreases to 64% and 43% when electronegative groups, F (**3h**) and CF_3 (**3i**), are introduced, respectively. Therefore, the activity follows the trends of 4-H(**3a**) ≈ 4-methyl (**3f**) ≈ 4-isopropyl (**3g**) > 4-F (**3h**) > 4-F (**3i**), while *trans*-1,4 selectivity is in the order of 4-CF_3 (**3h**) < 4-F (**3i**) < 4-H(**3a**) < 4-methyl (**3f**) < 4-isopropyl (**3g**). It can be deduced that the size of the substituents at the 4-position has a rather feeble effect on the steric nature of the active species, therefore, the *trans*-1,4selectivity varies only in a rather narrow range. Referring to catalytic activity, the alkyl substituent at the 4-position also has a negligible effect on the electronic nature of the active species, and the activity. Electron withdrawing groups, however reduce the electron density of the metal center and probably destablize the active site, diminishing the catalytic activity and reducing the polymer yield.

Combined with the effects of the 2-positoned substituents, it can be concluded that bulkiness at the 2-positions plays an important role in affecting the activity and selectivity, while tho seat the 4-positions, regardless of the nature and size, influence the polymer yield only.

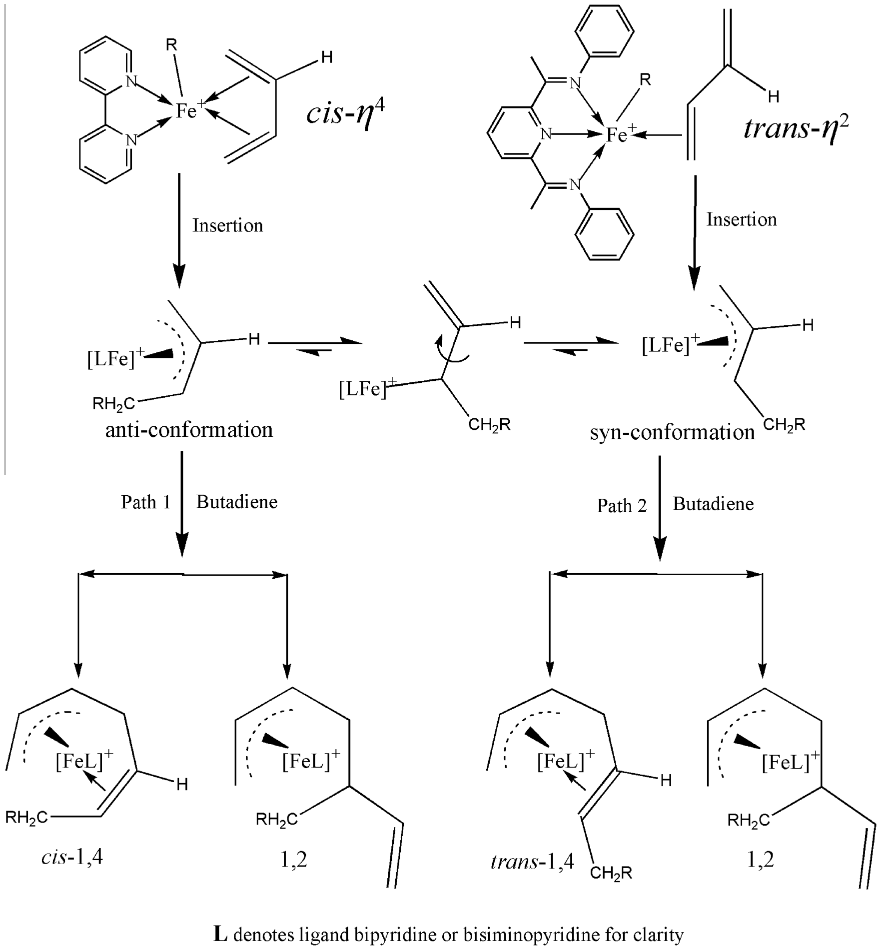
*3.2.3. Butadiene polymerization behavior by using complex **3a***

Besides the structure of the complexes, the polymerization conditions play an important role in controlling the activity, selectivity as well as the properties of the resulted polymer [17,19,21,48,49]. Herein, the influence of the reaction temperature is investigated by using complex **3a** as a precursor. The obtained results in Tables 4 show some interesting differences with the aforementioned iron catalysts [16–19]. The activity is dependent on the polymerization temperature. Maximal yield up to 99% is noticed at 20 °C, followed by a decrease with increasing temperature. It is most deduced that the lifetime of active site reaches maximum at 20 °C, then decreases with increasing temperature due to the deactivation of the active site. It is reported that for most iron-based catalysts, both catalytic selectivity and molecular weight of the resulting polymer decreases with increasing polymerization temperature, especially above room temperature, distinctively, both *trans*-1,4 selectivity and molecular weight of the obtained polymer increase with the polymerization temperature rising from −20 to 20 °C, and are kept as it increases further. The results demonstrate that the active site displays a superior tolerance to that found in the iron catalysts with bidentate ligands, and the latter has been shown that optimal activity and selectivity could not be reached simultaneously, for instance, selective polymerization is only performed at extremely low temperature (−78 °C), while the high activity appears at room temperature only [16–19]. It turns out that the ligand system employed here is capable of stabilizing the activated metal center in spite of the severe temperature variation.

With complex **3a** as a precursor, the effects of the Al/Fe molar ratio and the types of the alkyl aluminum on polymerization behavior are investigated (Table 5). With a variation of the Al/Fe molar ratio from 20 to 150, little influence on the selectivity, the activity, or even the M_n and M_w/M_n of the polymer can been seen, differentiating from the reported iron systems where either the activity or the molecular parameters of the polymer is governed by the cocatalyst concentration [18–21]. Similarly, no significant difference with respect to polymerization behaviors is apparent when Al^iBu_3, MMAO, MAO, or $AlEt_3$ is used as cocatalyst, respectively, with an exception that the M_n of the polymer observed in the $AlEt_3$ activated system is almost half of that found in the presence of Al^iBu_3. These results suggest the catalyst exhibits superior tolerance to the natures of the alkyl aluminum activators.

3.2.4. Mechanism study on trans-1,4 selectivity

It has been reported that there may be two types of active species which undergo different polymerization mechanisms in butadiene polymerization [50–56], as shown in Scheme 2 [57], according to the structure of the ligands. Iron catalysts such as the bidentate counterparts $FeCl_2(bipyridine)_2$ [19] and $FeEt_2(bipyridine)_2$ [18] tended to produce polybutadiene with mixed *cis*-1,4 and 1,2 selectivity, through the insertion of the monomer in an alternative mode to the iron anti-η^3-allyl intermediate by *cis*-η^4-coordination of butadiene with the central metal (Path 1) at room temperature. It is worthy to note that one bipyridine is assumed to



Scheme 2. The proposed mechanism for butadiene polymerization.

disassociate from metal center during the polymerization [19], otherwise, the electron number in iron(II) active species would surpass 18e, and such disassociation has also been deduced in $CrCl_2$ complexes with two bidentated phosphine ligands [6]. In comparing to complexes bearing a bidentate ligand, one more coordination site in the corresponding metal is occupied in case of those with a tridentate ligand, as the iron(III) is assumed to be reduced to the Fe(II) in the presence of cocatalyst. Thus, the syn-η^3-allyl polymer chain resulting from one double bond coordinated intermediate (*trans*-η^2coordination) (Scheme 2, path 2) is mainly produced, giving, ultimately, a *trans*-1,4 chain structure dominated polybutadiene. It is presumed that, by employing a tridentate ligand, the coordination mode of iron with monomer and the conformation of π-allyl polymer intermediate have been altered, and in turn, the microstructure of resulting polymer switches to *trans*-1,4 dominated.

4. Conclusion

Bis(imino)pyridyl iron(III) complexes have been synthesised, characterized and butadiene polymerization has been examined and discussed. The effects of the substituents at the 2-positions and the 4-position of the *N*-aryl moieties on the catalytic activity, selectivity and molecular weight of the resulting polymer have been explored from the viewpoint of both steric and electronic natures of the substituents. It has been proved that the complexes bearing a 2,6-bis(iminoethyl)pyridine tridentate ligand as precursors have a high tolerance to the variations of Al/Fe molar ratio, activator types and polymerization temperature. The high *trans*-1,4 selectivity can be ascribed to the predominately *trans*-η^2coordination of butadiene to the metal center.

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Appendix A. Supplementary material

CCDC 713160, 713933, 740169 contain the supplementary crystallographic data for **3a**, **3d** and **3f**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.047.

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