

1,3-Butadiene Polymerizations Catalyzed by Cobalt and Iron Dichloride Complexes Bearing Pyrazolyimine Ligands

Liang Fang^{a†}, Wen-Peng Zhao^{a,b†}, Chao Han^c, Chun-Yu Zhang^{a*}, Heng Liu^{a*}, Yan-Ming Hu^a, and Xue-Quan Zhang^a

^a CAS Key Laboratory of High-Performance Synthetic Rubber and its Composite Materials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c School of Materials Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China

Abstract A series of pyrazolyimine ligated Co(II) and Fe(II) complexes with general formula of $(\text{PhC}=\text{N}(\text{C}_6\text{H}_3(\text{R}_1)_2-2,6)(\text{C}_3\text{HN}_2(\text{R}_2)_2-3,5)\text{MtCl}_2$ ($\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{H}$, $\text{Mt} = \text{Co}$ (**1a**), **Fe** (**2a**); $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{Me}$, $\text{Mt} = \text{Co}$ (**1b**), **Fe** (**2b**); $\text{R}_1 = i\text{Pr}$, $\text{R}_2 = \text{H}$, $\text{Mt} = \text{Co}$ (**1c**), **Fe** (**2c**); $\text{R}_1 = i\text{Pr}$, $\text{R}_2 = \text{Me}$, $\text{Mt} = \text{Co}$ (**1d**), **Fe** (**2d**); $\text{R}_1 = i\text{Pr}$, $\text{R}_2 = \text{Ph}$, $\text{Mt} = \text{Co}$ (**1e**), **Fe** (**2e**)) were synthesized and thoroughly characterized. Determined by single crystal X-ray diffraction, complexes **1b** and **2b** revealed dimeric structures, in which distorted trigonal bipyramidal geometries were adopted for each metal centers. In the presence of ethylaluminum sesquichloride (EASC), all the cobalt complexes displayed high activities in 1,3-butadiene polymerization, affording polybutadienes with predominant *cis*-1,4 contents (up to 97.0%). Influences of ligand structure and polymerization parameters on catalytic performance were investigated systematically. For pyrazolyimine iron(II) dichloride complexes, the catalytic activities and microstructures of the resultant polybutadienes were highly dependent on ligand structures and polymerization conditions. For complex **2a**, changing cocatalyst from trialkyl aluminums to methyl aluminoxane (MAO) led to an shift of selectivity from high *cis*-1,4- to *trans*-1,4-/1,2- manner. Being activated by MAO, complexes **2a** and **2b** gave *trans*-1,4-/1,2- binary polybutadienes, while complexes **2c**, **2d**, and **2e** afforded *cis*-1,4- enriched polymers.

Keywords Late transition metal; Cobalt(II) complexes; Iron(II) complexes; Stereoselective polymerization; Polybutadiene

Citation: Fang, L.; Zhao, W. P.; Han, C.; Zhang, C. Y.; Liu, H.; Hu, Y. M.; Zhang, X. Q. 1,3-Butadiene polymerizations catalyzed by cobalt and iron dichloride complexes bearing pyrazolyimine ligands. *Chinese J. Polym. Sci.* 2019, 37, 462–470.

INTRODUCTION

The field of 1,3-butadiene polymerization using post-metallocene complexes has experienced tremendous progresses in the past three decades, spurred firstly by the aspiration of researchers to develop new non-metallocene catalytic systems, and secondly by the ever-growing of industrial interests.^[1–5] Up to date, diversified transition metal and lanthanide complexes have been designed, and some of them have been applied for practical industrial production.^[6–13] Among them, late-transition metal precatalyst is a continuous hotspot due to their earth abundance, ease of manipulation, eco-friendliness, and more importantly, their low-oxophilic properties, which enables the highly-active polymerization of olefin/diene monomer with polar comonomers to directly prepare functionalized polymers.^[14–17] For instance, Ricci and coworker reported that Co(II) and Fe(II) precursors, chelated by phosphorus and nitrogen ligands, were able to

produce high *cis*-1,4- or high 1,2-polybutadienes depending on the ligand designs.^[18,19] Shiono and Endo *et al.* demonstrated that Co(II)/MAO was a highly active and stereoselective system to give *cis*-1,4- polybutadienes, and in some cases controlled living polymerization was also observed.^[20,21] Mecking *et al.* reported that the cationic precursor, $[(\text{mesitylene})\text{Ni}(\text{allyl})^+][\text{BAR}_4^{\text{F}}^-]$, was capable of catalyzing the *cis*-1,4- selective copolymerization of 1,3-butadiene with functionalized dienes to directly prepare functionalized polybutadienes, which is of great importance from the viewpoint of practical applications.^[22,23] Besides the above chelating ligands, imine-based ligands are another important type of skeletons to support late-transition metal for selective polymerization of 1,3-dienes. Till now, various imine- (or imine analogue) based ligands have been employed to prepare corresponding late-transition metal complexes and subsequently initiate 1,3-butadiene polymerization, including bis(imino)pyridine,^[24–27] α -diimine,^[28] β -triketimine,^[29,30] bis(salicylaldimine),^[31,32] pyridine-2-imine,^[33,34] (1,10-phenanthroline-2-pyrazolyl),^[35] bis(oxazolonyl)pyridine,^[36] bis(imidazolyl)pyridine,^[37,38] bis(benzimidazolyl)amine,^[39] *etc.* Our interests are mainly focused on selective 1,3-butadiene polymerization using novel imine-based late-transition metal complexes. In our previous reports, we

* Corresponding authors: E-mail cyzhang@ciac.ac.cn (C.Y.Z.)

E-mail hengliu@ciac.ac.cn (H.L.)

† These authors contributed equally to this work.

Received September 27, 2018; Accepted November 3, 2018; Published online November 26, 2018

developed a new constructing unit, imidoylechloride, and a series of imidoylechloride-based complexes were successfully taped. Later 1,3-butadiene polymerization studies demonstrated much higher catalytic activities than that of chloride-free counterparts due to the enhanced electropositivity of the active species (Scheme 1a).^[40,41] Moreover, by using the nucleophilic reaction between imidoylechloride group and different nucleophiles, a series of bidentate and tridentate imidate-based late-transition metal complexes were designed, which also performed high activities and high *cis*-1,4- selectivities in 1,3-butadiene polymerization (Scheme 1b).^[42–44] As a continuous study of our previous research, in the present study, nucleophilic reaction between imidoylechloride and pyrazole was demonstrated, and a new family of pyrazolyimine Co(II) and Fe(II) complexes were subsequently prepared. The influences of the ligand skeleton and polymerization conditions on the 1,3-butadiene polymerization behaviors were further investigated.

EXPERIMENTAL

General Considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. The solvents were refluxed over CaH₂ or sodium-benzophenone and distilled prior to use. 1,3-Butadiene was obtained from Lanzhou Petrochemical Company and purified by passing through four columns packed with 4 Å molecular sieves and KOH. Other chemicals were commercially available and used without further purification. The ligands **a–e** were prepared according to previous reports.^[45,46]

¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) were recorded on a Varian Unity spectrometer in CDCl₃ at ambient temperature using tetramethylsilane as an internal standard.

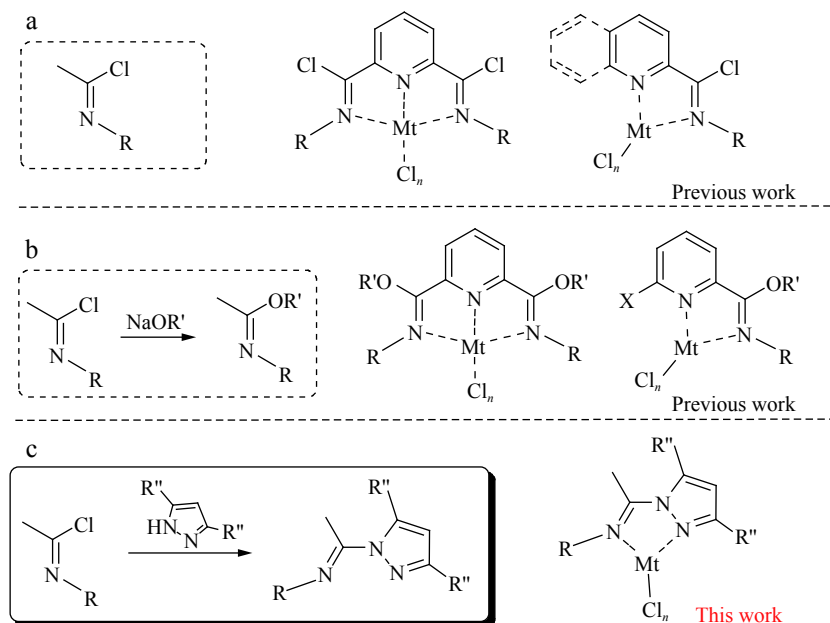
FTIR spectra were recorded using a BRUKER Vertex-70 FTIR spectrometer. Elemental analysis was performed on an elemental Vario EL spectrophotometer. The proportion of *cis*-1,4- and *trans*-1,4- units of the polymer was determined by FTIR spectra, ¹H-NMR, and ¹³C-NMR. The number-average molecular weights (*M_n*) and molecular weight distributions (*M_w*/*M_n*) of the polymers were measured at 30 °C by a gel permeation chromatography (GPC) instrument equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2THF), and a Waters 2414 refractive index detector. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL·min^{−1} against polystyrene as the calibration. Differential scanning calorimetry (DSC) analysis was performed on a Q20 DSC (TA instrument) under a nitrogen atmosphere. The samples were heated and cooled down at a rate of 10 °C·min^{−1}.

Synthesis and Characterization of the Complexes

All the cobalt(II) and iron(II) complexes were prepared in a similar method. A representative procedure for complex **2a** is described as follows. Ligand **a** (0.16 g, 0.5 mmol) was added into a 50 mL Schlenk flask and anhydrous FeCl₂ (0.063 g, 0.5 mmol), 2 mL of dry THF were sequentially added, and the resultant solution was stirred for 10 h. Partial removal of THF was carried out at the end of the reaction, and a large amount of Et₂O was added to precipitate the complex. The precipitates were filtered and dried under vacuum at 40 °C. Complexes **1a**, **1c**, **1d**, and **1e** were prepared according to previous reports.^[46]

Complex **1b**, yield 83.3%. FTIR (KBr, ν, cm^{−1}): 3109, 3004, 2956, 2924, 1611, 1589, 1567, 1494, 1459, 1446, 1385, 1365, 1258, 1212, 1173, 1159, 1114, 1050, 986, 918, 838, 797, 780, 744, 704. Anal. Calcd. for C₂₀H₂₁Cl₂CoN₃ (432.1): C, 55.45; H, 4.89; N, 9.70. Found: C, 55.42; H, 4.81; N 9.63.

Complex **2a**, yield 74.9%. FTIR (KBr, ν, cm^{−1}): 3138,



Scheme 1 Imidoylechloride-derived ligands and their corresponding late-transition metal complexes

2974, 1637, 1396, 1206, 1164, 1097, 944, 784, 703. Anal. Calcd. for $C_{18}H_{17}Cl_2FeN_3$ (402.1): C, 53.77; H, 4.26; N, 10.45. Found: C, 51.50; H, 4.08; N, 10.01.

Complex **2b**, yield 83.3%. FTIR (KBr, ν , cm^{-1}): 3109, 2924, 1611, 1567, 1494, 1385, 1258, 1159, 986, 780, 704. Anal. Calcd. for $C_{20}H_{21}Cl_2FeN_3$ (430.15): C, 55.84; H, 4.92; N, 9.77. Found: C, 55.76; H, 4.91; N, 9.73.

Complex **2c**, yield 80.2%. FTIR (KBr, ν , cm^{-1}): 2966, 2929, 1617, 1559, 1508, 1459, 1202, 1160, 1058, 913, 759, 696. Anal. Calcd. for $C_{22}H_{25}Cl_2FeN_3$ (458.21): C, 57.67; H, 5.50; N, 9.17. Found: C, 57.73; H, 5.49; N, 9.13.

Complex **2d**, yield 85.1%. FTIR (KBr, ν , cm^{-1}): 2982, 2866, 1610, 1563, 1465, 1327, 1241, 1152, 1035, 971, 821, 706. Anal. Calcd. for $C_{24}H_{29}Cl_2FeN_3$ (486.26): C, 59.28; H, 6.01; N, 8.64. Found: C, 59.35; H, 6.08; N, 8.68.

Complex **2e**, yield 74.9%. FTIR (KBr, ν , cm^{-1}): 2961, 2865, 1636, 1596, 1463, 1176, 1098, 965, 833, 760, 691. Anal. Calcd. for $C_{34}H_{33}Cl_2FeN_3$ (610.4): C, 66.90; H, 5.45; N, 6.88. Found: C, 66.98; H, 5.46; N, 6.89.

X-ray Crystallographic Studies

Crystals for X-ray analyses were obtained as described above. Data collections were performed at low or room temperature on a Bruker SMART APEX diffractometer with a CCD area detector using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved using the 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. CCDC numbers were 1868306 and 1868307 for complexes **1b** and **2b**, respectively.

General Procedure for the Solution Polymerization of 1,3-Butadiene

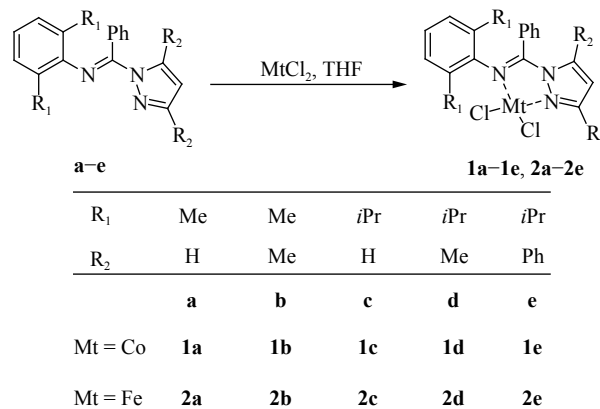
A typical procedure for the polymerization is as follows (run 16). A toluene solution (10 mL) of 1,3-butadiene (1 g, 0.0185 mol) was added into a moisture-free ampule bottle preloaded with complex **2b** (3.4 mg, 0.009 mmol), and then EASC (0.46 mmol) was injected to initiate the polymerization at 20 °C. After 30 min, methanol was added 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. Filtered and dried under vacuum at 40 °C, polybutadiene was resulted at a constant weight (0.772 g, 77.2%).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Co(II) and Fe(II) Complexes

The pyrazolylimine ligands bearing different substituents were prepared according to previous reports by reacting imidoylchloride with substituted pyrazoles.^[45,46] The Co(II) and Fe(II) complexes, **1a–1e** and **2a–2e**, were prepared by stoichiometric reaction of anhydrous $CoCl_2$ or $FeCl_2$ with the

corresponding ligands in THF, and subsequently precipitated by excessive Et_2O (Scheme 2). All the complexes were thoroughly characterized by FTIR and elemental analysis. Complexes **1b** and **2b** were further characterized by single crystal X-ray diffraction analysis, and the molecular structures are shown in Figs. 1 and 2.



Scheme 2 Synthetic procedures for complexes **1a–1e** and **2a–2e**

Single crystal of **1b** was obtained by slow diffusion of Et_2O into its CH_2Cl_2 saturated solution, and the structure is shown in Fig. 1(a), from which a centrosymmetric dimer structure could be clearly observed. Each metal center adopts a distorted trigonal bipyramid geometry, in which Cl(1), N(1), and one chloride atom Cl(2) form the equatorial plane, and N(3) and another chloride atom Cl(2) occupy the axial positions. The two equatorial planes in the dimeric structure are parallel to each other (Fig. 1b). The cobalt atoms locate at 0.127 Å above the equatorial plane, and the intramolecular distance of two cobalt atoms Co–Co is 3.577 Å, which is slightly shorter than the value observed in its binuclear Ni(II) counterparts. For the coordination geometry, the axial bond of Co1–Cl2 is much longer than the other axial bond of Co–N3 (2.4603(6) Å versus 2.1359(17) Å), which plays an important role in distorting the trigonal bipyramid structure. The coordination bond lengths between the cobalt and nitrogen atoms vary in the range of 2.0899(17)–2.1359(17) Å, and those of Co–Cl bond vary in the range of 2.2719(6)–2.4603(6) Å. In complex **1b**, the diisopropylphenyl planes are approximately perpendicular to the pyrazol/Co coordination planes, with a dihedral angle of 85.65°, quite similar to its Ni(II) analogues.

Single crystal of complex **2b** was obtained by slow diffusion Et_2O into its saturated THF solution, and the structure is shown in Fig. 2(a). Similar to complex **1b**, complex **2b** also displays centrosymmetric dimer structure, in which each iron center adopts a distorted trigonal bipyramid geometry. The two equatorial planes built up by Cl(1), Cl(2), and N(2) are almost parallel to each other (Fig. 2b). Also, the axial bond of Fe1–Cl1, with the length of 2.5272(8) Å, is much longer than the other axial bond Fe1–N1, with value of 2.1596(19) Å, which mainly caused the distorted trigonal bipyramid geometry around the metal center. The diisopropyl substituted phenyl ring is oriented approximately perpendicular to

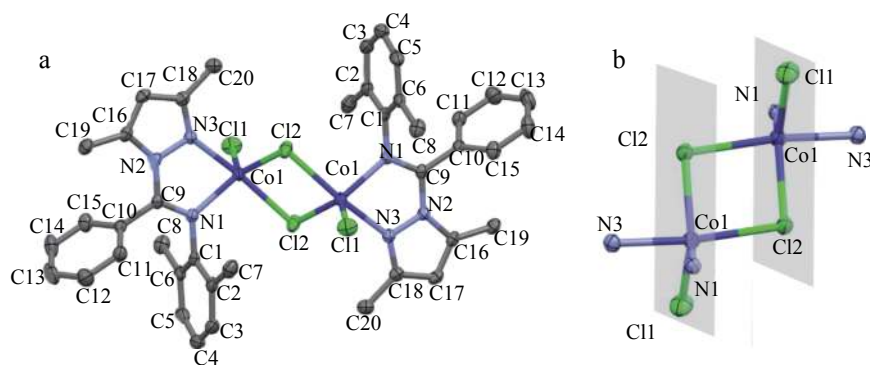


Fig. 1 (a) Molecular structure of complex **1b**; (b) Equatorial planes for the two cobalt metal centers (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Co1–N1 2.0899(17) Å, Co1–N3 2.1359(17) Å, Co1–Cl1 2.2719(6) Å, Co1–Cl2 2.3493(6) Å, Co1–Cl2 2.4603(6) Å, N1–Co1–N3 75.22(6)°, N1–Co1–Cl1 112.85(5)°, N3–Co1–Cl1 92.50(5)°, N1–Co1–Cl2 122.92(5)°, N3–Co1–Cl2 91.99(5)°, Cl1–Co1–Cl2 123.27(3)°, N1–Co1–Cl2 95.31(5)°, N3–Co1–Cl2 168.89(5)°, Cl1–Co1–Cl2 98.38(2)°, Cl1–Co1–Cl2 83.93(2)°, Co1–Cl2–Co1 96.07(2)°

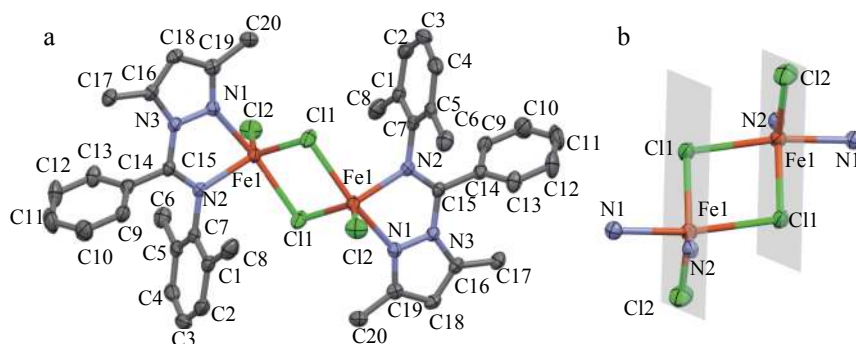


Fig. 2 (a) Molecular structure of complex **2b**; (b) Equatorial planes for the two iron metal centers (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Fe1–N1 2.1596(19) Å, Fe1–N2 2.1625(19) Å, Fe1–Cl2 2.2759(9) Å, Fe1–Cl1 2.3836(8) Å, Fe1–Cl1 2.5272(8) Å, Cl1–Fe1 2.3836(8) Å, N1–Fe1–N2 73.67(7)°, N1–Fe1–Cl2 96.44(6)°, N2–Fe1–Cl2 113.97(6)°, N1–Fe1–Cl1 93.06(6)°, N2–Fe1–Cl1 121.16(6)°, Cl2–Fe1–Cl1 124.51(3)°, N1–Fe1–Cl1 164.72(5)°, N2–Fe1–Cl1 96.39(5)°, Cl2–Fe1–Cl1 98.24(3)°, Cl1–Fe1–Cl1 82.09(3)°, Fe1–Cl1–Fe1 97.91(3)°

the pyrazol/Co coordination plane with a dihedral angle of 85.88°. The intramolecular distances of Fe–Fe (3.705 Å) well corresponds to the values (3.744(1) Å and 3.678(2) Å) in dinickel complexes, albeit much longer than that of the dicobalt counterpart **1b**.

1,3-Butadiene Polymerizations

1,3-Butadiene polymerization with Co(II) complexes

1,3-Butadiene polymerization with the cobalt precatalysts was firstly evaluated to optimize the polymerization conditions. As the results summarized in Table 1, when using cobalt complex **1c** as a precatalyst, aluminum chloride compounds, including ethylaluminum sesquichloride (EASC) and diethylaluminum chloride (DEAC), were proved to be highly efficient cocatalysts in initiating 1,3-butadiene polymerization, affording polybutadienes with 84.6% and 94.5% yields, respectively. By contrast, methyl aluminoxane (MAO)-based system was proved to be less-efficient, affording only 21.6% yield under identical conditions. In strikingly different, when being activated by AlEt₃ and

Al(^{*i*}Bu)₃, **1c** behaved almost inactive and only gave rise to traces amount of polybutadiene products, probably due to the over-reduction of cobalt active species caused by the strong reducing abilities of these two compounds. Similar phenomena were also observed in other cobalt complexes mediated diene polymerizations. Kinetic studies using **1c**/EASC system revealed that the polymerization yields could reach up to *ca.* 90% within 30 min, which is the most active system in the present studies. As for the microstructures of the resultant polybutadienes obtained above, both MAO and aluminum chloride based systems led to high *cis*-1,4-products, with the content ranging from 93.7% to 96.3%.

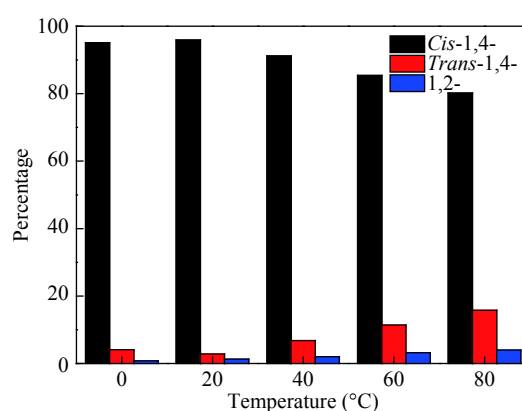
The influence of temperature on polymerization behaviors was further investigated with the **1c**/EASC system. According to runs 10–13 in Table 1, the catalytic activities increased significantly from 0 °C to 40 °C, while further elevating the temperature hardly changed the polymerization yields. It is worth noting that complex **1c**, different from the previously reported cobalt complexes that suffered severe decay of activities at elevated temperatures,^[34,47] displayed

Table 1 1,3-Butadiene polymerization under different conditions with **1c**/EASC system ^a

Run	Al	<i>T</i> (°C)	[Al]/[Co]	Yield (%)	<i>M_n</i> ^b × 10 ^{−4} (g·mol ^{−1})	<i>M_w</i> / <i>M_n</i> ^b	Microstructure ^c (%)		
							<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
1	MAO	20	50	21.6	4.6	4.3	93.5	4.4	2.1
2 ^d	AlEt ₃	20	50	Trace	n.d.	n.d.	n.d.	n.d.	n.d.
3 ^d	Al(^{<i>i</i>} Bu) ₃	20	50	Trace	n.d.	n.d.	n.d.	n.d.	n.d.
4	AlEt ₂ Cl	20	50	84.6	9.3	4.6	95.7	2.2	2.1
5	EASC	20	50	94.5	6.8	4.9	94.3	4.1	1.6
6	EASC	20	10	21.7	21.4	2.8	96.3	2.5	1.2
7	EASC	20	20	86.8	15.9	4.4	95.4	3.4	1.2
8	EASC	20	30	89.4	8.9	6.6	94.7	3.8	1.5
9	EASC	20	100	95.0	8.7	5.3	93.7	4.3	2.0
10	EASC	0	30	18.6	10.6	2.8	95.1	3.7	1.2
11	EASC	40	30	97.1	6.4	5.7	91.2	6.5	2.3
12	EASC	60	30	98.9	5.5	7.1	85.4	11.4	3.2
13	EASC	80	30	99.5	4.6	8.7	80.2	15.8	4.0

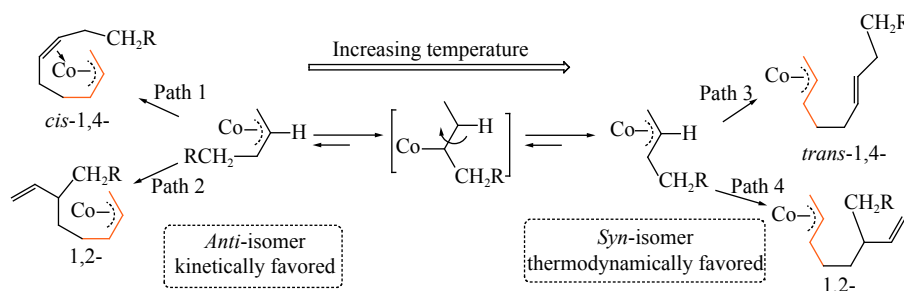
^a Polymerization conditions: in toluene, [Bd]/[Co] = 2000, [Al]/[Co] = 50, [Bd] = 1.85 mol·L^{−1}, 30 min; ^b Determined by GPC eluted with THF (polystyrenes as standards); ^c Determined by IR and NMR; ^d n.d. for not determined

high thermo-stability, and almost quantitative conversions were observed at temperature as high as 80 °C. On the other hand, with an increasing temperature, the molecular weights of the resultant polybutadienes decreased dramatically from 10.6×10^4 to 4.6×10^4 due to the enhanced chain transfer reaction at high temperatures. Meanwhile, The *cis*-1,4- content of the resulting polymer decreased from 95.1% to 80.2%, and the *trans*-1,4- and 1,2- contents increased from 3.7% and 1.2% to 15.8% and 4.0%, respectively, when the temperature increased from 0 °C to 70 °C (Fig. 3). This tendency might be attributable to the facilitated *anti-syn* isomerization through π - σ rearrangement at high temperatures.^[5] In principle, the polybutadienyl chain end can be coordinated to the metal center through π -allylic form, which include *anti*- and *syn*- conformations; the former isomer produces *cis*-1,4- and 1,2- units, while the latter isomer generates *trans*-1,4- and 1,2- moieties (Fig. 4). At lower temperature, path 1 was kinetically favored due to the π -back-bonding effect, and the 1,3-butadiene monomers tended to form *cis*-1,4- structure. With an elevated temperature, *anti-syn* isomerization through the π - σ -rearrangement was gradually facilitated as the *syn*- isomer was more thermodynamically stable, and the contents of *trans*-1,4- and 1,2- units were thus increased. Fig. 5 provides the DSC curves of the polybutadienes obtained at various temperatures. Polybutadiene obtained at 0 °C displayed the lowest *T_g* (−104.60 °C), and rising polymerization temperature resulted in the higher *T_g* of the resulting polymer due to the increased *trans*-1,4- and 1,2-

**Fig. 3** Changes in the microstructures of polybutadienes with the variation of reaction temperature

contents.

The influence of ligand structure on 1,3-butadiene polymerization was examined (Table 2). Complexes **1a** and **1b**, bearing 2,6-dimethylphenyl moiety on imine-nitrogen position and Me/H, Me/Me on pyrazoyl ring, displayed moderate catalytic activities, affording polybutadienes in 85.1% and 77.2% yields, respectively. Complexes **1c** and **1d** bearing 2,6-diisopropylphenyl moiety on imine-nitrogen position demonstrated much higher activities, giving 94.5% and 90.4% yields under identical conditions. However, increasing the steric congestion on the 3,5- position of pyrazoyl ring resulted in lower activities probably due to the inaccessibility

**Fig. 4** Proposed scheme for 1,3-butadiene polymerization (Yellow lines stand for the newly inserted 1,3-butadiene monomer.)

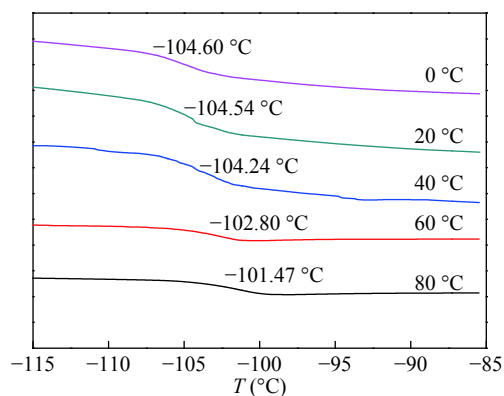


Fig. 5 DSC curves of the polybutadienes obtained at various temperatures

Table 2 1,3-Butadiene polymerization with different Co(II) complexes^a

Run	Cat.	Yield (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b	Microstructure ^c (%)		
					<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
14	1a	85.1	7.6	4.8	94.9	3.8	1.3
15	1b	77.2	12.5	3.2	96.0	3.0	1.0
16	1c	94.5	6.8	4.9	94.3	4.1	1.6
17	1d	90.4	9.8	4.8	95.9	2.8	1.3
18	1e	79.8	24.4	4.4	97.0	1.9	1.1

^a Polymerization conditions: in toluene at 20 °C for 30 min, [Bd]/[Co] = 2000, [Al]/[Co] = 50, [Bd] = 1.85 mol·L⁻¹; ^b Determined by GPC eluted with THF (polystyrenes as standards); ^c Determined by IR and NMR

ies of 1,3-butadiene monomer to cobalt center caused by higher steric bulkiness. It is worth noting that the ligand substituent posed little influence on selectivity, and all the complexes gave high *cis*-1,4-polybutadienes (94.9%–97.0%). Fig. 6 provides the NMR spectra obtained for **1e**/EASC system.

1,3-Butadiene polymerization with Fe(II) complexes

The catalytic performances of pyrazolylimine iron(II) dichloride complexes was investigated next, and the results are summarized in Table 3. Different from cobalt dichloride

counterparts, the iron(II) dichloride complexes could be activated by trialkyl aluminum compounds and subsequently initiate 1,3-butadiene polymerization, albeit with relative lower yields. In the presence of Al(*i*Bu)₃, AlMe₃, AlEt₃, and Al(Oct)₃, complex **2a** was able to polymerize 1,3-butadiene in the yields of 40.6%, 32.8%, 49.0%, and 58.7%, respectively. The most efficient cocatalyst was proved to be MAO, which could activate **2a** and subsequently polymerize 1,3-butadiene in almost quantitative yield (97.4%) under identical polymerization parameters. The type of cocatalyst also exerted significant influence on the microstructures of the resultant polybutadienes. Activated by trialkyl aluminum compound, *cis*-1,4-/1,2- binary polymers were obtained with *cis*-1,4- as the dominant microstructure; however, MAO-mediated systems gave rise to *trans*-1,4-/1,2- binary polymers with 1,2- units as the primary structure. Additionally, the amounts of MAO hardly influenced the microstructures. Similar to the cobalt(II)-mediated systems, elevating the polymerization temperature also posed great influence on the microstructures of the resultant polybutadienes. Monotonous decrease of *cis*-1,4- content from 21.4% to 3.0%, together with an increment of *trans*-1,4- content from 2.1% to 45.9%, was observed when increasing the temperature from 0 °C to 70 °C, which is also due to the facilitated *anti*-*syn* isomerization at high temperatures (Fig. 5).

As the results summarized in Table 4, ligand structure remarkably affected the catalytic activities and microstructures of the resultant polybutadienes. The highest activity was displayed in **2a**/MAO system, and other complexes only revealed moderate activities with 42.6%, 31.6%, and 37.6% yields for **2b**, **2c**, and **2d** mediated systems, respectively. The most inferior activity was observed in **2e** system, which only showed 29.2% conversion under identical condition, probably due to the highly steric congested ligand substituents. On the other hand, complexes **2a** and **2b** bearing 2,6-dimethylphenyl moiety on imine-nitrogen position eventually gave *trans*-1,4-/1,2- binary polybutadienes, while complexes **2c**, **2d**, and **2e** produced *cis*-1,4-enriched polybutadienes.

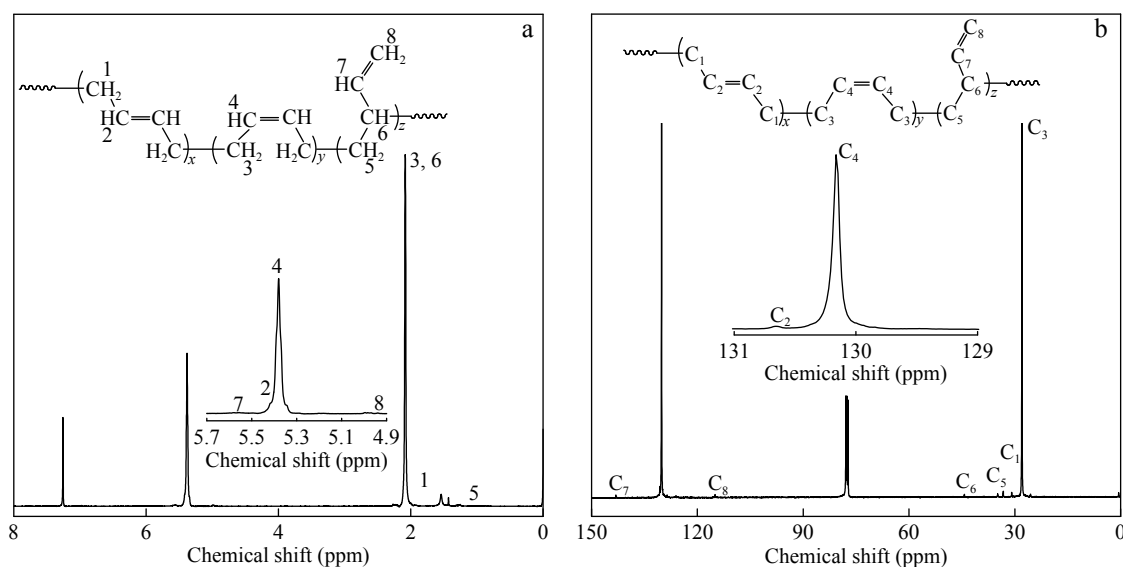


Fig. 6 NMR spectra of the polybutadienes obtained by **1e**/EASC system

Table 3 1,3-Butadiene polymerization under different conditions using **2a**^a

Run	Al	Al/Fe	T (°C)	Yield (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b	Microstructure ^c (%)		
							<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
19	Al(<i>i</i> Bu) ₃	20	30	40.6	3.6	2.5	67.5	3.4	29.1
20	AlMe ₃	20	30	32.8	4.2	2.7	79.3	2.4	28.3
21	AlEt ₃	20	30	49.0	2.7	2.8	72.6	4.1	23.3
22	Al(Oct) ₃	20	30	58.7	2.9	2.4	67.9	3.5	28.6
23	MAO	100	30	97.4	7.2	2.0	7.8	29.5	62.7
24	MAO	50	30	57.9	2.9	2.6	8.2	30.5	61.3
25	MAO	150	30	97.6	7.5	2.3	7.9	28.4	63.7
26	MAO	200	30	98.5	8.3	2.6	7.9	29.1	63.0
27	MAO	100	0	50.6	4.9	1.8	21.4	8.1	70.5
28	MAO	100	50	99.6	15.4	2.6	3.7	41.7	54.6
29	MAO	100	70	98.9	12.1	2.8	3.0	45.9	51.1

^a Polymerization conditions: in toluene, [Bd]/[Fe] = 2000, [Bd] = 1.85 mol·L⁻¹, 4 h; ^b Determined by GPC eluted with THF (polystyrenes as standards); ^c Determined by IR and NMR

Table 4 1,3-Butadiene polymerization with different Fe(II) complexes^a

Run ^a	Cat.	Yield (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b	Microstructure ^c (%)		
					<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
30	2a	97.4	7.2	2.0	7.8	29.5	62.7
31	2b	42.6	3.1	1.7	9.9	53.8	36.3
32	2c	31.6	5.6	1.6	61.2	13.9	24.9
33	2d	37.6	4.3	1.8	77.6	7.5	14.9
34	2e	29.2	4.5	1.7	72.1	19.0	8.9

^a Polymerization conditions: in toluene, [Bd]/[Fe] = 2000, [MAO]/[Fe] = 100, [Bd] = 1.85 mol·L⁻¹, 30 °C, 4 h; ^b Determined by GPC eluted with THF (polystyrenes as standards); ^c Determined by IR and NMR

Fig. 7 provides the ¹H-NMR spectra of polybutadienes obtained from complexes **2a–2e**, from which an obvious resonance of 1,2-structure was observed for **2a** and **2b** mediated systems. DSC was employed to examine the thermal behaviors of these polybutadienes. As the thermograms shown in Fig. 8, *cis*-1,4-enriched polybutadienes obtained from complexes **2c**, **2d**, and **2e** displayed very low glass transition temperatures, of -86.31, -91.98, and -91.63 °C, respectively. With the increasing contents of 1,2- and *trans*-1,4- microstructures, as observed from complexes **2a** and **2b**, *T_g* increased to -49.55 and -68.94 °C, respectively.

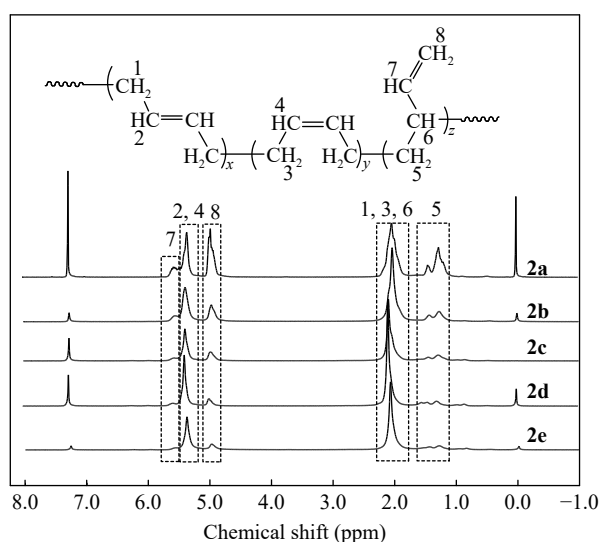


Fig. 7 ¹H-NMR spectra of the polybutadienes obtained by different iron complexes

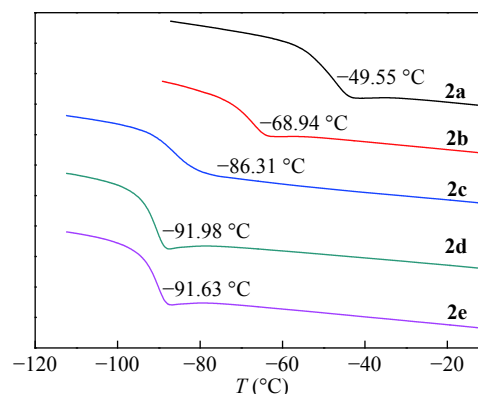


Fig. 8 DSC curves of the polybutadienes obtained by different Fe(II) complexes

CONCLUSIONS

Cobalt(II) and iron(II) complexes supported by pyrazolylimine ligands were synthesized, and their catalytic behaviors towards 1,3-butadiene polymerization were systematically investigated. Being activated by EASC, the cobalt(II) complexes displayed the high activities, affording polybutadienes with the predominant *cis*-1,4- contents up to 97.0%. Increasing the temperature resulted in the gradual decrement of molecular weights due to facilitated chain transfer reactions, together with monotonously decreasing *cis*-1,4- units caused by facilitated *anti-syn* isomerization. For iron complexes, the catalytic activities and microstructures of the resultant polybutadienes were highly dependent on the ligand structures and polymerization conditions. Being activated by MAO, complexes **2a** and **2b** gave rise to *trans*-1,4-/1,2-binary polybutadienes, while complexes **2c**, **2d**, and **2e** led to

cis-1,4- enriched polymer products. Studies on various cocatalysts revealed that for complex **2a**, changing cocatalyst from MAO to trialkyl aluminum compounds could alter the selectivities from binary *trans*-1,4-/1,2- manner to high *cis*-1,4- manner.

ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (No. 2015CB654700 (2015CB654702)) and the National Natural Science Foundation of China (No. 21801236).

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