#### Inorganica Chimica Acta 414 (2014) 8-14

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

## Synthesis of cationic cobalt(II) complexes and their efficiency as catalysts for the polymerization of 1,3-butadiene

Li Liu<sup>a,b</sup>, Xu Zhang<sup>a,b</sup>, Heng Liu<sup>b</sup>, Xuequan Zhang<sup>b</sup>, Guangping Sun<sup>a,\*</sup>, Hexin Zhang<sup>b,\*</sup>

<sup>a</sup> Materials Science and Engineering, Jilin University, Changchun 130022, PR China <sup>b</sup> Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

#### ARTICLE INFO

Article history: Received 2 November 2013 Received in revised form 3 January 2014 Accepted 6 January 2014 Available online 25 January 2014

Keywords: Cobalt Catalyst 1,3-Butadiene Polybutadiene Polymerization mechanism

1. Introduction

### ABSTRACT<sup>1</sup>

A series of novel cationic cobalt(II) compounds accompanied by various counter ions ( $[BF_4]^-, [PF_6]^-, [SbF_6]^-$ ) and N-bearing ligands (1,10-phenanthroline, bipyridine, benzimidazole, and imidazole) were synthesized. Neutral compounds, CoCl<sub>2</sub>-nLigands, were prepared as reference compounds. All the compounds were characterized using IR spectral analysis and elemental analysis and some of the compounds were further characterized by single-crystal X-ray diffraction analysis. The synthesized compounds were evaluated as precursors for butadiene polymerization in conjunction with ethylaluminum sesquichloride as a cocatalyst, and the polymerization mechanism was proposed to involve anionic coordination polymerization. The active centers of the catalysts were cationic in nature, and the catalytic activities were affected by the electronegativity of the counter ion.

© 2014 Elsevier B.V. All rights reserved.

Regio- and/or stereo-selective polybutadiene have been extensively and diversely applied throughout the rubber industry since the discovery of Ziegler–Natta-type catalyst systems [1–9]. Hence, investigation of butadiene polymerization, structures of catalyst precursors and catalyst-polymer correlations has served as a fascinating and challenging subject over the past decades and has promoted studies of catalyst design and catalysis mechanisms. Recently, late transition metal catalysts have initiated a completely new catalytic domain and have attracted a significant amount of interest due to their simple synthesis, stability and negligible environmental impact [10–21]. However, some late transition metal catalysts suffer from low activity, comparatively low *cis*-1,4 selectivity, and uncertain catalytic mechanism. Therefore, efficient catalysts that can produce polybutadiene with a high *cis*-1,4 content are highly desirable.

Metallocenes are known to show much higher catalytic activity toward olefin polymerization as compared to the Zielger–Natta catalyst [22–24]. A plausible explanation for this difference is the formation of a cationic active metal center in the metallocene catalyst activated with methylaluminoxane or borates [25–29], which

E-mail addresses: sungp@jlu.edu.cn (G. Sun), polyhx@ciac.ac.cn (H. Zhang).

<sup>1</sup> Phen, 1,10-phenanthroline; Bipy, bipyridine; BZI, benzimidazole; Im, imidazole; EASC, ethylaluminum sesquichloride; GPC, gel permeation chromatography.

increases the coordination and insertion rates of the olefin monomer during the polymerization process. In our previous research [30], a titanium-based Ziegler–Natta catalyst with a cationic active metal center was prepared via modification of the commercial Ziegler–Natta catalyst, and the catalytic activity was found to drastically increased after the modification.

Herein, we report for the first time, highly active cationic cobalt(II) catalysts. The effects of the catalyst structure (e.g., counter ions, ligands) and reaction conditions on the polymerization were studied. Furthermore, a plausible catalysis mechanism was put forward to explain the differences between the traditional and cationic cobalt(II) catalysts.

#### 2. Experimental

#### 2.1. Materials and methods

Cobalt carbonate (CoCO<sub>3</sub>), tetrafluoroboric acid (HBF<sub>4</sub>), hexafluorophosphoric acid (HPF6), and fluoroantimonic acid (HSbF<sub>6</sub>) were purchased from Alfa Aesar, China. 1,10-phenanthroline (Phen), bipyridine (Bipy), benzimidazole (BZI), and imidazole (Im) were supplied by J&K, China. Ethylaluminum sesquichloride (EASC) was purchased from Akzo Nobel, USA. Polymerization-grade butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through four columns packed with molecular sieves and solid potassium hydroxide. Toluene was distilled by heating to reflux in the presence of sodium and benzophenone. Other chemicals were used as received. Infrared (IR) spectra were







<sup>\*</sup> Corresponding authors. Tel.: +86 431 85262889; fax: +86 431 85262274 (H.X. Zhang).

obtained on a Bruker Vertex-70 FT-IR spectrophotometer. The weight-average molecular weights ( $M_w$ ) and polydispersity ( $M_w$ / $M_n$ ) of the resulting polymers were measured at 30 °C by gel permeation chromatography (GPC), using a chromatographic system equipped with a Waters 515 HPLC pump, four columns, and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Crystals for X-ray diffraction were obtained as described in the Results and discussion section. Data collection for compound **1b** was perfrormed at 22 °C, and data for the other compounds were collected at -88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector. Determination of the crystal class and unit cell parameters was carried out using the SMART program package. The raw

frame data were processed by SAINT and SADABS to yield the reflection data file. The structures were determined using the SHELXTL program. Refinement was performed on  $F^2$  anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

#### 2.2. Syntheses and characterization of compounds

A general synthetic route to cobalt(II) compounds is shown in Scheme 1. The typical synthetic procedure for **1a** is as follows: Cobalt(II) tetrafluoroborate hexahydrate (0.5 g, 1.47 mmol), prepared by mixing excess CoCO<sub>3</sub> with HBF<sub>4</sub> in H<sub>2</sub>O at ambient temperature, was mixed with Phen (0.79 g, 4.39 mmol) in methanol (20 mL) to afford a yellow transparent solution. Compound **1a** was obtained



Scheme 1. Syntheses of cobalt(II) compounds.

#### Table 1

Crystal data and structure refinements of compounds 1a, 1b, and 4a.

	4a	1a	1b
Formula	$C_{27}H_{23}C_{12}CoN_4$	$C_{38}H_{29.5}B_2CoF_8N_6$	$C_{31}H_{31}B_2CoF_8N_8$
Molecular weight	533.32	810.73	1496.38
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ
Color of crystal	yellow	purple	yellow
a (Å)	10.7724	11.1961	10.3908
b (Å)	10.8378	12.9138	10.6832
c (Å)	10.9523	14.3453	19.3985
α (°)	85.6420	81.2415	87.055
β (°)	84.4350	75.9587	75.488
γ (°)	78.6430	68.5142	71.841
V (Å <sup>3</sup> )	1245.60	1867.7	1980.01
Ζ	2	2	2
$D_{\text{calc.}}$ (mg/m <sup>3</sup> )	1.442	1.442	1.255
Absorption coefficient (mm <sup>-1</sup> )	0.926	0.538	0.502
F(000)	548.0	825.0	764.0
Crystal size (mm)	$0.28\times0.2\times0.12$	$0.29 \times 0.16 \times 0.10$	$0.24 \times 0.18 \times 0.10$
$\theta$ (°)	1.87-26.04	1.47-25.35	1.08-26.19
No. of reflections collected	6826	9766	11218
No. of independent reflections	4806	6739	7833
No. of data/restraints/params	4806/0/308	6739/12/534	7833/0/452
Goodness-of-fit (GOF) on $F^2$	1.054	1.007	1.087
$R_1(1 > 2\sigma(1))$	0.0460	0.0666	0.0690
wR <sub>2</sub>	0.1217	0.2030	0.1612

Table 2
Selected bond distances (Å) and angles (°) of cobalt compounds <b>1a</b> , <b>1b</b> , and <b>4a</b> .

1a		1b		4a	
Co1-N1	2.137 (3)	Co1-N4	1.985 (2)	Co1-N2	2.142 (3)
Co1-N6	2.137 (3)	Co1-N8	1.994 (2)	Co1-N1	2.159 (2)
Co1-N4	2.140 (3)	Co1-N2	1.991 (2)	Co1-N4	2.161 (2)
Co1-N5	2.142 (3)	Co1-N6	2.003 (2)	Co1-N3	2.194 (2)
Co1-N2	2.142(3)			Co1-Cl1	2.3915 (7)
Co1-N3	2.150(3)			Co1-Cl2	2.4213 (7)
N1-Co1-N6	96.19(13)	N4-Co1-N8	107.75 (9)	N2-Co1-N1	77.55 (10)
N1-Co1-N4	165.80 (13)	N4-Co1-N2	106.96 (10)	N2-Co1-N4	164.99 (8)
N6-Co1-N4	95.25 (13)	N8-Co1-N2	114.82 (9)	N1-Co1-N4	92.35 (10)
N1-Co1-N5	95.54 (13)	N4-Co1-N6	113.37 (9)	N2-Co1-N3	91.25 (8)
N6-Co1-N5	78.13 (14)	N8-Co1-N6	105.57 (9)	N1-Co1-N3	84.83 (8)
N4-Co1-N5	95.02 (13)	N2-Co1-N6	108.55 (9)	N4-Co1-N3	76.64 (8)
N1-Co1-N2	78.36 (14)			N2-Co1-Cl1	94.43 (6)
N6-Co1-N2	94.68 (13)			N1-Co1-Cl1	169.93 (8)
N4-Co1-N2	92.35 (13)			N4-Co1-Cl1	94.26 (6)
N5-Co1-N2	170.12 (13)			N3-Co1-Cl1	89.32 (5)
N1-Co1-N3	92.17 (13)			N2-Co1-Cl2	96.43 (6)
N6-Co1-N3	167.84 (13)			N1-Co1-Cl2	88.92 (7)
N4-Co1-N3	77.95 (13)			N4-Co1-Cl2	94.42 (6)
N5-Co1-N3	92.30 (13)			N3-Co1-Cl2	168.83 (6)
N2-Co1-N3	95.66 (13)			Cl1-Co1-Cl2	98.12 (3)





Fig. 1. X-ray structure of 1a. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

by extracting and subsequently removing the solvent in vacuo. The neutral compounds were also prepared for comparison. All products were dried at 50°C in a vacuum drying oven and obtained as air-stable powders in high yields (62.8–90.7%).

*Tri*(1,10-*phenanthroline*)*cobalt*(*II*) *tetrafluoroborate* (**1***a*): Yellow powder, 90.7% yield. IR (KBr, cm<sup>-1</sup>): 1624(m), 1581(w), 1518(s), 1495(w), 1425(s), 1340(w), 1304(w), 1062(s), 847(s), 724(s), 521(w). *Anal.* Calc. for  $C_{36}H_{24}B_2CoF_8N_6$ : C, 55.92; H, 3.13; N, 10.87. Found: C, 55.87; H, 3.37; N, 10.95%.

*Tri*(1,10-*phenanthroline*)*cobalt*(*II*) *hexafluorophosphate* (**2a**): Yellow powder, 87.2% yield. IR (KBr, cm<sup>-1</sup>): 1624(w), 1581(w), 1517(s), 1427(s), 1346(w), 1142(m), 1104(m), 861(m), 847(s), 725(w), 482(w), 463(w). *Anal.* Calc. for  $C_{36}H_{24}CoF_{12}N_6P_2$ : C, 48.61; H, 2.72; N, 9.45. Found: C, 48.65; H, 2.80; N, 9.43%.

*Tri*(1,10-phenanthroline)cobalt(II) fluoroantimonic (**3a**): Yellow powder, 82.3% yield. IR (KBr, cm<sup>-1</sup>): 2364(w), 1624(w), 1518(s), 1491(w), 1426(s), 1103(w), 1084(w), 846(m), 726(m). *Anal.* Calc.

for  $C_{36}H_{24}CoF_{12}N_6Sb_2$ : C, 40.37; H, 2.26; N, 7.85. Found: C, 40.45; H, 2.32; N, 7.83%.

ment ellipsoids are drawn at the 50% probability level.

*Tetra*(*Benzimidazole*)*cobalt*(*II*) *tetra*fluoroborate (**1b**): Purple powder, 62.8% yield. IR (KBr, cm<sup>-1</sup>): 1623(w), 1597(w), 1493(w), 1420(s), 1302(m), 1270(w), 1250(s), 1083(s), 741(s), 614(m), 521(w). *Anal.* Calc. for  $C_{28}H_{20}B_2CoF_8N_8$ : C, 47.97; H, 2.88; N, 15.98. Found: C, 47.94; H, 2.30; N, 15.95%.

*Tri(Bipyridine)cobalt(II) tetrafluoroborate* (**1***c*): Yellow powder, 79.2% yield. IR (KBr, cm<sup>-1</sup>): 1637(w), 1598(s), 1575(m), 1492(m), 1474(s), 1442(s), 1315(s), 1284(w), 1062(s), 774(s), 737(m), 521(w). *Anal.* Calc. for  $C_{30}H_{24}B_2CoF_8N_6$ : C, 51.39; H, 3.45; N, 11.99. Found: C, 51.33; H, 3.54; N, 11.21%.

*Tetra*(*Imidazole*)*cobalt*(*II*) *tetra*fluoroborate (**1d**): Pink powder, 85.6% yield. IR (KBr, cm<sup>-1</sup>): 1589(s), 1536(w), 1430(m), 1330(w), 1298(w), 1256(w), 1070(s), 770(s), 664, 621(s), 521(w). *Anal.* Calc. for  $C_{28}H_{20}B_2CoF_8N_4$ : C, 28.78; H, 2.42; N, 22.37. Found: C, 28.81; H, 2.39; N, 22.43%.



Fig. 3. X-ray structure of 4a. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Bis(1,10-phenanthroline)cobalt(II) chloride (**4a**): Yellow powder, 76.9% yield. IR (KBr, cm<sup>-1</sup>): 1624(w), 1584(w), 1516(s), 1425(s), 1342(w), 1305(w), 1143(m), 1103(m), 850(m), 725(s), 641(w), 422(w). Anal. Calc. for  $C_{24}H_{16}C_{12}CoN_4$ : C, 58.80; H, 3.29; N, 11.43. Found: C, 55.84; H, 3.22; N, 11.58%.

Bis(Benzimidazole)cobalt(II) chloride (**4b**): Purple powder, 80.2% yield. IR (KBr, cm<sup>-1</sup>): 1622(m), 1597(m), 1492(s), 1460(m), 1414(s), 1300(s), 1271(s), 1246(s), 1114(m), 1002(m), 977(m), 742(s), 618(m), 418(s). Anal. Calc. for  $C_{15}H_{13}C_{12}CoN_4$ : C, 47.52; H, 3.46; N, 14.78. Found: C, 47.80; H, 3.50; N, 14.69%.

*Bis(Bipyridine)cobalt(II) chloride (4c)*: Brown powder, 72.1% yield. IR (KBr, cm<sup>-1</sup>): 1595(s), 1574(m), 1490(m), 1473(s), 1440(s), 1315(s), 1174(m), 1157(m), 1060(m), 1037(s), 1018(m), 785(s), 766(s), 737(s), 650(m), 627(m), 420(m). *Anal.* Calc. for C<sub>20-</sub>H<sub>16</sub>C<sub>12</sub>CoN<sub>4</sub>: C, 54.32; H, 3.65; N, 12.67. Found: C, 54.40; H, 3.66; N, 12.62%.

Bis(Imidazole)cobalt(II) chloride (**4d**): Blue powder, 85.4% yield. IR (KBr, cm<sup>-1</sup>): 1539(m), 1487(m), 1327(m), 1256(m), 1107(w), 1068(s), 940(m), 852(w), 665(s), 614(s). Anal. Calc. for  $C_6H_6C_{12}$ -CoN<sub>4</sub>: C, 27.30; H, 2.29; N, 21.22. Found: C, 27.34; H, 2.31; N, 21.20%.

#### 2.3. Procedure for butadiene polymerization

All manipulations were carried out under a dry nitrogen atmosphere. Butadiene polymerization was conducted as follows: **1a** was added as a solid to a moisture-free ampoule capped with a

able 3	
ffects of various counter ions and ligands on butadiene polymerizatio	n.

rubber septum. Then a solution of butadiene in toluene (20 mL, 0.1 g/mL) was injected into the ampoule. After that, EASC (0.37 mL, 0.5 mol/L) was added to the ampoule to initiate the polymerization. The polymerization was carried out at 25 °C for 40 min and quenched by adding ethanol containing 2,6-di-tert-butyl-4-methylphenol (1.0% v/v) as a stabilizer. The product was dried overnight in a vacuum oven (yield: 0.642 g, 32.1%).

#### 3. Results and discussion

#### 3.1. Preparation and characterization of compounds

Cationic cobalt(II) compounds were prepared by the reaction of cobalt tetrafluoroborate with different N-bearing ligands in methanol. The products were isolated as air-stable powders in good yields and characterized by IR spectra and X-ray analysis. The IR spectra of the cobalt(II) compounds were recorded in the region 4000–400 cm<sup>-1</sup> region, and tentative assignments were made on the basis of published data [31-34]. In the IR spectra of the free ligands, the C=N stretching frequencies appeared at 1561-1618 cm<sup>-1</sup>. In compounds, the C=N stretching vibrations shifted toward lower frequencies and were greatly reduced in intensity, which suggested the coordination interaction between the nitrogen atoms and the metal ion. IR peaks of other cobalt compounds were in good agreement with the literature values [35,36]. In order to establish the coordination mode of the compounds, the structures of compounds 1a, 1b, and 4a were confirmed by X-ray diffraction analysis. The crystallographic data of the compounds and the collection and refinement parameters are summarized in Tables 1 and 2 and their crystal structures are depicted in Figs. 1–3. The  $[Co(Phen)_3]^{2+}$  cation coordinated by six N atoms of Phen displayed a distorted octahedral coordination geometry and was balanced by two [BF<sub>4</sub>] counter anions, both of which had a slightly distorted tetrahedral coordination geometry. The mean deviation of the cobalt atom from the equatorial plane (N(1)-N(3)-N(4)-N(6)) was 0.176 Å, and all the bond angles in the equatorial plane were in the range of 77.97–96.18° (N(1)–Co–N(3), 92.13°; N(3)-Co-N(4) 77.97°; N(4)-Co-N(6), 95.26°; N(1)-Co-N(6), 96.18°). The axial Co-N bonds subtended an angle of  $170.11^{\circ}$  (N(2)–Co–N(5)), and the axial bond lengths of the Co–N bonds were both 2.142 Å. Compound 4a (Fig. 3) had similar structural features as the cation of 1a, and the coordination geometry around the cobalt center was distorted octahedron. The N1, N3, Cl1, and Cl3 atoms were located in the equatorial plane with a mean deviation of 0.164 Å, and the equatorial angles N(1)-Co-N(3), N(3)-Co-Cl(1), Cl(1)-Co-Cl(2), and Cl(2)-Co-N(1) were 84.82°, 89.32°, 98.12°, and 88.93° respectively. As expected, the

Entry <sup>a</sup>	Catalyst	Yield (%)	Microstructure <sup>b</sup>	Microstructure <sup>b</sup>			$M_{\rm w}/M_{\rm n}^{\rm c}$
			cis-1,4 (%)	trans-1,4 (%)	1,2 (%)		
1	$[Co(Phen)_3][BF_4]_2$	99.9	92.9	5.0	2.1	47.9	3.8
2	[Co(Phen) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	93.9	89.9	7.6	2.5	20.6	4.6
3	$[Co(Phen)_3][SbF_6]_2$	93.0	93.6	7.6	2.4	26.5	4.0
4	$[Co(Phen)_2]Cl_2$	88.0	86.4	9.8	3.8	17.3	5.3
5	$[Co(Bipy)_3][BF_4]_2$	86.6	94.8	3.8	1.4	42.6	3.7
6	[Co(Bipy) <sub>2</sub> ]Cl <sub>2</sub>	80.5	84.5	11.5	4.0	21.5	4.3
7	$[Co(BZI)_4][BF_4]_2$	95.3	95.2	3.2	1.6	50.0	3.6
8	[Co(BZI) <sub>2</sub> ]Cl <sub>2</sub>	89.0	88.5	8.5	3.0	19.8	3.9
9	$[Co(Im)_4][BF_4]_2$	79.0	94.7	3.9	1.4	57.5	3.6
10	$[Co(Im)_2]Cl_2$	65.5	86.6	11.0	2.4	23.4	4.1

<sup>a</sup> Polymerization conditions: [Bd] = 0.1 g/mL, [Bd]/[Co] = 2000, [Al]/[Co] = 50, toluene, 50 °C, 40 min.

<sup>b</sup> Determined by FTIR.

<sup>c</sup> Determined by GPC.

Table 4

Entry <sup>a</sup>	[Al]/[Co]	[Bd]/[Co]	Yield (%)	Microstructure <sup>b</sup>			$M_{\rm w}^{\rm c}~( imes 10^{-4})$	$M_{\rm w}/M_{\rm n}^{\rm c}$
				cis-1,4 (%)	trans-1,4 (%)	1,2 (%)		
11	10	1000	49.4	96.7	2.1	1.2	51.5	2.7
12	10	2000	32.1	96.8	1.7	1.5	62.2	2.3
13	10	3000	5.8	94.5	3.4	2.1	63.1	2.3
14	30	2000	49.8	96.6	2.0	1.4	63.6	2.4
15	50	2000	78.0	95.8	2.5	1.7	63.5	3.0
16	70	2000	79.5	95.5	2.6	1.9	64.9	2.8
17	100	2000	84.8	95.5	2.6	1.9	65.3	3.3

Tuble 4						
Effects of [Al]/[Co]	and [Bd]/[Co]	on butadiene	polymerization	behaviors wit	th [Co(Phen)3]	[BF4]2/EASC

<sup>a</sup> Polymerization conditions: [Bd] = 0.1 g/mL, 25 °C, toluene, 40 min.

<sup>b</sup> Determined by FTIR.

<sup>c</sup> Determined by GPC.

Co–Cl bond lengths of **4a** (Co–Cl(1) = 2.3915 Å, Co–Cl(1) = 2.4213 Å) were shorter than the Co···B bond distances of **1a** (Co···B(1) = 7.401 Å, Co···B(2) = 5.776 Å). Similarly, compound **1b** consisted of two  $[BF_4]^-$  anions, and the  $[Co(BZI)_4]^{2+}$  cation was coordinated by four N-atoms of BZI. The geometries of the cation and anion were both confirmed as a slightly distorted tetrahedron. Steric and electronic effects of the various ligands had significant influence on the electropositivity of the center metal, which affected the interaction between the metal and counter ions. The different interactions between the cation and the anion were reflected in the difference in the Co···B distance. The Co···B distances in **1b** (Co···B(1) = 5.299 Å, Co···B(2) = 5.585 Å) were shorter than those in **1a** (Co···B(1) = 7.401 Å, Co···B(2) = 5.776 Å), presumably due to the stronger coordination between the cobalt center and

Fig. 4. Plots of yield and cis-content against [Al]/[Co] ratio.

Table 5

Effects of Polymerization Temperature and Time on Butadiene Polymerization with [Co(Phen)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub>/EASC

the N atoms of the Phen ligand. These results indicated that the metal center of the synthesized cobalt compounds was cationic in nature, whereas that in the traditional cobalt chloride compound was not. We tentatively hypothesized that such compounds probably catalyzed butadiene polymerization more effectively and rapidly during the chain initiation and propagation.

# 3.2. Butadiene polymerization of compounds activated by alkylaluminium chlorides

As shown in Table 2, butadiene polymerization initiated by the cobalt(II) compounds was carried out in conjunction with EASC as a cocatalyst. The catalytic activity of the cationic cobalt(II) compounds in the polymerization of butadiene was higher, as compared to that of the traditional cobalt(II) compound. Furthermore, the catalytic activity of the compounds was affected by the corresponding counter ions (Entries 1-4) was in the following order:  $[BF_4] > [PF_6] > [SbF_6] > Cl.$  Additionally, the *cis*-1,4 content of the polybutadiene prepared using cationic cobalt(II) catalysts (Entries 1-3) was higher as compard to that of the polybutadiene prepared using the traditional cobalt(II) compound (Entry 4). This indicated that the catalytic activity and stereo-selectivity of the cationic compounds with counter ions were superior to that of cobalt chloride compound in the polymerization of butadiene. In addition,  $M_w$  of the polymers obtained from the cationic cobalt(II) compounds (Entries 1-3) was higher than that of the polybutadiene prepared using the traditional cobalt(II) compound. The higher  $M_{\rm w}$  of obtained polybutadiene could be ascribed to the higher chain propagation rate and/or lower chain transfer rate of the cationic cobalt(II) compounds. The effect of N-bearing ligands on the butadiene polymerization was also studied. As shown in Table 3, the cis-1,4 content and  $M_w$  of the polymers prepared using the cationic cobalt(II) compounds (Entry1, Entry 4-10) were more

Entry <sup>a</sup>	<i>T</i> (°C)	<i>t</i> (min)	Yield (%)	Microstructure <sup>b</sup>			$M_{\rm w}^{\rm c}~( imes 10^{-4})$	$M_{\rm w}/M_{\rm n}^{\rm c}$
				cis-1,4 (%)	trans-1,4 (%)	1,2 (%)		
20	0	40	-	-	-	-	-	-
21	25	40	32.1	96.8	1.7	1.5	62.2	2.3
22	50	40	80.3	91.5	5.0	3.5	34.9	3.9
23	70	40	82.5	87.0	8.5	4.4	29.1	5.7
24	90	40	91.0	81.0	13.6	5.4	27.0	7.0
25	25	20	13.5	96.8	2.0	1.3	52.5	2.3
26	25	80	53.7	95.8	2.5	1.7	67.1	2.9
27	25	120	64.1	95.2	3.1	1.7	65.2	2.9
28	25	240	78.5	94.9	3.1	1.9	53.2	3.4

<sup>a</sup> Polymerization Conditions:[Bd] = 0.1 g/mL, [Bd]/[Co] = 2000, [Al]/[Co] = 10, toluene, 40 min.

<sup>b</sup> Determined by FTIR.

<sup>c</sup> Determined by GPC.



Fig. 5. Plots of molecular weight and polydispersity against polymerization temperature.

higher than those in the case of the traditional one. The highest yield was achieved with compound **1a**, and hence, this compound was chosen as the optimal catalyst for further investigations.

Butadiene polymerization was carried out with varying [Al]/ [Co] molar ratios and catalyst concentrations; the results are shown in Table 4. The catalytic activity gradually decreased with higher [Bd]/[Co] ratios, and the maximum yield (49.4%; Entry 11) was observed at the lowest [Bd]/[Co] ratio (1000). Higher activities were observed with increased ratios of [Al]/[Co] (10–100; Entries



Fig. 6. Plots of yield and cis-content against polymerization time.

12, 14–17). At a [Al]/[Co] molar ratio of 50, the conversion reached 78.0% (Entry 15). Further increase in the [Al]/[Co] molar ratio to 100 produced a slight increase in the catalytic activity (Entries 16, 17; Fig. 4). In addition, the  $M_w$  and polydispersity of the resultant polybutadiene were less affected by the cocatalyst concentration, which indicated that the transfer to the cocatalyst was very weak.

The effects of polymerization temperature and time on the microstructure of the polymer were examined and the results are summarized in Table 5. The yield of the polymer increased observably with increased temperature (Entries 20–24), while the  $M_w$  drastically decreased and the distribution became broader (Fig. 5). This result suggested that rate of the chain transfer reaction increased with increasing temperature. In addition, the *cis*-1,4 content of the polymer decreased with increasing temperature, whereas the *trans*-1,4 and 1,2 content increased correspondingly. As shown in Fig. 6, the polymer yield increased with increasing polymerization time, while the *cis*-1,4 content slightly decreased (Entries 25–28).

#### 3.3. Mechanism of butadiene polymerization

Cationic cobalt(II) catalysts with counter ions produced polybutadiene in a high yield and cis-1,4 content as compared to the traditional cobalt(II) catalysts. Compound 1a was used as an example to explain the catalytic mechanism in the case of the novel cationic cobalt compounds. Porri et al. demonstrated that the active species of alkylated cobalt compounds were monovalent in hydrocarbonbased solvents [37]. The polymerization mechanism in the case of the traditional cobalt catalyst and cationic cobalt catalysts are given in Scheme 2. The polymerization occurred via two steps after the catalyst was activated by the cocatalyst. In the first step, the butadiene monomer coordinated to the active center, followed by the migratory insertion of the coordinated monomer into the cobalt-carbon bond. In the migratory insertion step (second step), a vacant coordination site was regenerated, which enabled further chain propagation. Compared to the traditional cobalt catalyst, the active center of the cationic cobalt catalyst showed very strong negative electron affinity, which increased the coordination and insertion rate of the butadiene monomer [38-40]. Additionally, we hypothesized that the cationic cobalt center (electron deficient) would lead to an attractive force to the C=C double bond of the penultimate monomer unit. Therefore, the polybutadiene afforded by the cationic cobalt(II) catalyst had a higher cis-1,4 content as compared to polybutadiene prepared by using the traditional catalyst.



Scheme 2. The proposed polymerization mechanism of (a) traditional cobalt(II) catalyst and (b) cationic cobalt(II) catalyst toward butadiene polymerization.

#### 4. Conclusion

A new and effective methodology toward improving the performance of a traditional cobalt(II) catalyst was established. A series of highly active cationic cobalt(II) catalysts were successfully synthesized. The active centers of the catalysts prepared were cationic in nature, whereas the active center of the traditional catalyst was not. In addition, the catalytic activity and stereoselectivity of the cationic compounds were superior to those of cobalt chloride in the polymerization of butadiene. The mechanism of butadiene polymerization with the novel cationic cobalt(II) catalyst system presumably involved anionic coordination polymerization.

#### Acknowledgement

The work was supported by the Specialized Research Fund for the Doctoral Program of Higher Education of China (20120061110030) and Science and Technology Development Plan of Jilin Province (20130102007JC).

#### **Appendix A. Supplementary material**

CCDC 873097, 873098 and 949093 contains the supplementary crystallographic data for **1a**, **1b** and **4a**. 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 http://dx.doi.org/10.1016/j.ica.2014.01.012.

#### Reference

- [1] G. Natta, L. Porri, A. Carbonaro, Makromolekul Chem 77 (1964) 126.
- [2] G. Ricci, M. Battistella, L. Porri, Macromolecules 34 (2001) 5766.
- [3] G. Ricci, A. Forni, A. Boglia, M. Sonzogni, Organometallics 23 (2004) 3727.
  [4] G. Ricci, A. Forni, A. Boglia, A. Sommazzi, F. Masi, J. Organomet. Chem. 690
- (2005) 1845.[5] S. Kaita, Y. Takeguchi, Z.M. Hou, M. Nishiura, Y. Doi, Y. Wakatsuki, Macromolecules 36 (2003) 7923.
- [6] S. Kaita, Z.M. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 9078.

- [7] S. Kaita, Z.M. Hou, M. Nishiura, Y. Doi, J. Kurazumi, A.C. Horiuchi, Y. Wakatsuki, Macromol Rapid Commun 24 (2003) 180.
- [8] R. Cariou, J. Chirinos, V.C. Gibson, G. Jacobsen, A.K. Tomov, M.R.J. Elsegood, Macromolecules 42 (2009) 1443.
- [9] Y.C. Jang, P. Kim, H. Lee, Macromolecules 35 (2002) 1477.
- [10] V. Appukuttan, L. Zhang, C.S. Ha, I. Kim, Polymer 50 (2009) 1150.
- [11] W. Gao, D.M. Cui, J. Am. Chem. Soc. 130 (2008) 4984.
- [12] A. Miyazawa, T. Kase, K. Hashimoto, J.C. Choi, T. Sakakura, J. Ji-zhu, Macromolecules 37 (2004) 8840.
- [13] S. Kaita, M. Yamanaka, A.C. Horiuchi, Y. Wakatsuki, Macromolecules 39 (2006) 1359.
- [14] Y. Nakayama, Y. Baba, H. Yasuda, K. Kawakita, N. Ueyama, Macromolecules 36 (2003) 7953.
- [15] L.H. Cao, W.M. Dong, L.S. Jiang, X.Q. Zhang, Polymer 48 (2007) 2475.
- [16] D.R. Gong, W.M. Dong, Y.M. Hu, J.F. Bi, X.Q. Zhang, L.S. Jiang, Polymer 50 (2009) 5980.
- [17] Y.M. Hu, W.M. Dong, L.S. Jiang, X.Q. Zhang, G. Yu, L.H. Cao, Chinese J. Catal. 25 (2004) 664.
- [18] D.C.D. Nath, T. Shiono, T. Ikeda, Macromol. Chem. Phys. 203 (2002) 1171.
- [19] D.C.D. Nath, T. Shiono, T. Ikeda, Macromol. Chem. Phys. 204 (2003) 2017.
- [20] Y.C. Jang, P.S. Kim, H.Y. Jeong, H. Lee, J. Mol. Catal. A-Chem. 206 (2003) 29.
- [21] W. Zhang, W.J. Zhang, W.H. Sun, Prog. Chem. 17 (2005) 310.
   [22] W. Kaminsky, J. Chem. Soc. Dalton (1998) 1413.
- [23] W. Kaminsky, M. Arndt, I. Beulich, Abstr. Pap. Am. Chem. S, 213 (1997) 10-Pmse.
- [24] H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. 34 (1995) 1143.
- [25] C. Sishta, R.M. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112.
- [26] X.M. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623.
- [27] G.G. Hlatky, R.R. Eckman, H.W. Turner, Organometallics 11 (1992) 1413.
- [28] G.G. Hlatky, H.W. Turner, R.R. Eckman, J. Am. Chem. Soc. 111 (1989) 2728.
- [29] W. Kaminsky, A. Bark, R. Steiger, J. Mol. Catal. 74 (1992) 109.
- [30] H.X. Zhang, H. Zhang, C.Y. Zhang, C.X. Bai, X.Q. Zhang, J. Polym. Sci. Polym. Chem. 50 (2012) 4805.
- [31] R.P. Sharma, A. Singh, P. Brandao, V. Felix, P. Venugopalan, J. Mol. Struct. 920 (2009) 119.
- [32] R.P. Sharma, A. Singh, P. Venugopalan, W.T.A. Harrison, J. Mol. Struct. 994 (2011) 6.
- [33] R. Sharma, R.P. Sharma, B.M. Kariuki, J. Fluorine Chem. 129 (2008) 325.
- [34] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan, J.M. Salas, M. Quiros, J. Fluorine Chem. 126 (2005) 1543.
- [35] S. Brownstein, J. Chem. Soc.-Chem. Commun. (1980) 149.
- [36] S. Youngme, N. Chaichit, Polyhedron 21 (2002) 247.
- [37] L. Porri, A. Carbonaro, Makromolekul. Chem. 60 (1963) 236.
- [38] S. Tobisch, R. Taube, Organometallics 18 (1999) 3045.
- [39] S. Tobisch, R. Taube, Organometallics 18 (1999) 5204.
- [40] G.A. Aminova, G.V. Manuiko, G.I. Litvinenko, G.S. D'yakonov, V.L. Zolotarev, A.G. Filipova, T.V. Ignashina, V.V. Davydova, O.V. Antonova, Russ. J. Appl. Chem. 75 (2002) 1146.