



ORIGINAL ARTICLE

# Synthesis and butadiene polymerization behaviors of cationic cobalt-based catalyst



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*Cis*-1,4

**Abstract** A series of cationic cobalt-based compounds bearing different neutral N-bearing ligands (1,10-phenanthroline, bipyridine, benzimidazole, terpyridine) and anionic ligands (trifluoromethanesulfonate, methanesulfonate) were synthesized and the simple compound,  $\text{Co}(\text{Phen})_2\text{Cl}_2$ , was also prepared as a reference compound. All the compounds were characterized along with infrared spectra analysis and some of them were further confirmed by single crystal X-ray crystallographic analysis. Upon activation with ethylaluminum sesquichloride, these cationic cobalt(II) compounds showed high catalytic activities for butadiene polymerization. The detailed investigations were carried out to disclose the influence of various polymerization conditions, sterical and electronic parameters of the ligands on their performing activities of the compounds.

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## 1. Introduction

Regio- and/or stereospecific polymerization of 1,3-butadiene, i.e. 1,4-*cis* [1,14,20,12], 1,4-*trans* [18,5,3,2], 1,2-*vinyl* [16,7] polymerization, is a subject of substantial interest in both academic

and industrial fields. In particular, selective 1,4-*cis*-specific polymerization has attracted much attention, because the resultant polybutadiene exhibits excellent elastic properties and is useful as synthetic rubber. Jang [11] reported that the microstructure of polybutadiene, within a wide range, from high *cis*-1,4 (96.6%) to high 1,2 content (95.8%), could be gradually tuned by changing substituted groups on ligand. In the subsequent years, many researches were focused on the modification of sterical and electronic properties of the substituent on the ligands [8], [10], [9,17,6]. However, the effect of anion structure of cationic cobalt-based catalyst on the butadiene polymerization behaviors was less mentioned. Additionally, Childers [4] reported that, in the case of soluble cobalt initiators, for polymerizing butadiene to a high *cis*-1,4 configuration

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the propagation step was occurred through an intermediate carbonium ion.

Therefore, herein for the first time, a series of cationic cobalt-based compounds supported by different anionic ligands ( $[\text{TfO}]^-$ ,  $[\text{MSA}]^-$ ) were designed and employed as catalyst precursors for butadiene polymerization. The effects of catalyst structure (e.g. ligands, counter anions) and polymerization conditions on polymerization behaviors were studied. In addition, the polymerization mechanism was also put forward to explain the differences between the traditional and cationic cobalt-based catalyst.

## 2. Experimental

### 2.1. Materials

Cobalt carbonate ( $\text{CoCO}_3$ ), trifluoromethanesulfonic acid (HTfO) and methanesulfonic acid (MSA) were purchased from Alfa Aesar, China. 1,10-phenanthroline (Phen), bipyridine (Bipy), benzimidazole (BZI) and terpyridine (Terpy) were supplied by J&K, China. Ethylaluminum sesquichloride (EASC) was commercially available from Akzo Nobel, USA. Polymerization grade butadiene was purchased from Jinzhou Petrochemical Corporation, China and purified by passing through four columns packed with molecular sieves and solid potassium hydroxide and toluene was freshly distilled over calcium hydride for 3 h and distilled before use. All solvents used were purified in the standard manner.

### 2.2. Syntheses and characterization of compounds

A general synthetic route for cobalt-based compounds is shown in Scheme 1. A typical synthetic procedure for **1b** is as follows: cobalt(II) trifluoromethanesulfonate hexahydrate was prepared by reaction of excess cobalt carbonate powder with trifluoromethanesulfonic acid at room temperature. The aqueous solution of cobalt trifluoromethanesulfonate hexahydrate, obtained by filtering out superfluous solid cobalt carbonate powder, was concentrated and dried at 50 °C in vacuo. The final product **1b** was obtained by drying as air-stable powder in high yields (65.2–90.3%) in vacuo after mixing cobalt trifluoromethanesulfonate hexahydrate (0.43 g, 0.93 mmol) and Phen (0.5 g, 2.8 mmol) in methanol (20 mL). The compound **2c** was also prepared as a contrast.

#### 2.2.1. Benzimidazole cobalt(II) trifluoromethanesulfonate (**1a**)

Purple powder, 90.3% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1623(m), 1609(w), 1600(w), 1507(m), 1455(m), 1175(s), 1116(m),

1030(s), 1008(m), 980(m), 910(w), 755(m), 740(s), 642(s), 621(w), 573(m), 515(s).

#### 2.2.2. 1,10-phenanthroline cobalt(II) trifluoromethanesulfonate (**1b**)

Yellow powder, 86.9% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1627(m), 1606(w), 1582(m), 1519(s), 1497(w), 1427(s), 1344(w), 1275(s), 1223(m), 1155(s), 1103(m), 1030(s), 868(m), 847(s), 776(w), 727(s), 636(s), 572(m), 517(m).

#### 2.2.3. Bipyridine cobalt(II) trifluoromethanesulfonate (**1c**)

Yellow powder, 84.6% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1604(m), 1597(m), 1575(w), 1568(w), 1492(w), 1473(s), 1444(s), 1315(w), 1226(s), 1103(w), 1064(w), 1029(s), 766(s), 737(s), 652(w), 637(s), 574(m), 515(s).

#### 2.2.4. Terpyridine cobalt(II) trifluoromethanesulfonate (**1d**)

Dark brown powder, 65.2% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1601(m), 1575(w), 1561(w), 1450(w), 1474(m), 1454(m), 1264(s), 1226(m), 1154(s), 1141(s), 1095(w), 1031(s), 1016(w), 787(s), 765(s), 752(w), 738(w), 650(w), 635(s), 573(m), 518(m).

#### 2.2.5. 1,10-phenanthroline cobalt(II) methanesulfonate (**2b**)

Yellow powder, 86.9% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1625(w), 1607(w), 1585(m), 1520(s), 1429(s), 1494(w), 1463(w), 1191(s), 1102(w), 1057(s), 849(s), 785(s), 772(s), 749(m), 726(s), 716(s), 538(m), 525(m).

#### 2.2.6. 1,10-phenanthroline cobalt(II) chloride (**2c**)

Yellow powder, 77.9% yield. IR (KBr,  $\text{cm}^{-1}$ ): 1624(w), 1584(w), 1516(s), 1425(s), 1342(w), 1305(w), 1143(m), 1103(m), 850(m), 725(s), 641(w), 422(w).

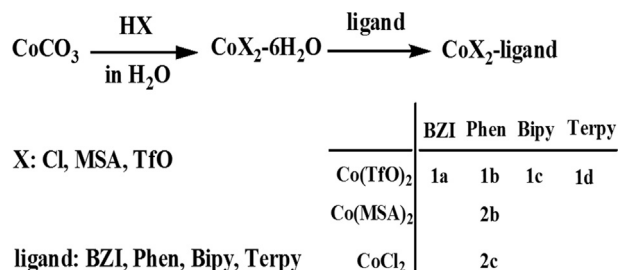
### 2.3. Procedure for butadiene polymerization

All manipulations were carried out under a dry nitrogen atmosphere. A typical procedure for the polymerization is as follows: compound **1b** was added to an ampoule capped with a septum. Then, a toluene solution of butadiene (20 mL, 0.1 g/mL) was injected into the ampoule. Catalyst components, EASC (0.37 mL, 0.5 mol/L), was consecutively introduced to the ampoule at designed ratios to initiate polymerization. The polymerization was maintained at 20 °C for 2.5 h and was quenched by adding ethanol containing 2,6-di-tert-butyl-4-methylphenol (1.0%) as a stabilizer. Polybutadiene was obtained after being dried in vacuum dry at 50 °C to constant weight (1.618 g, 80.9%).

## 3. Results and discussion

### 3.1. Preparation and characterization of compounds

Cationic Co-based compounds were prepared by reaction of cobalt trifluoromethanesulfonate ( $\text{Co}(\text{TfO})_2$ ) with N-bearing donors in methanol. The resultant compounds were isolated as air-stable powders in good yields and characterized by infrared spectra. The IR spectra of free ligands showed that the C=N stretching frequencies appeared at 1561–1618  $\text{cm}^{-1}$ . In compounds, the C=N stretching vibrations were shifted toward lower frequencies and greatly reduced in intensity, which



Scheme 1 Syntheses of cationic cobalt compounds.

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