



Pyridine–oxazoline and quinoline–oxazoline ligated cobalt complexes: Synthesis, characterization, and 1,3-butadiene polymerization behaviors



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ABSTRACT

A series of cobalt complexes supported by pyridine–oxazoline (Pyox) and quinoline–oxazoline (Quox) were synthesized. Determined by single crystal X-ray crystallography, complexes **6a** and **7c** adopted distorted octahedron and trigonal bipyramid geometries, respectively, while complex **6b** existed as an ion pair comprised of $[\text{CoL}_2]^{2+}$ and $[\text{CoCl}_4]^{2-}$, in which the cationic and anionic moieties displayed distorted octahedron and tetrahedral geometries, respectively. Upon activation with ethylaluminum sesquichloride (EASC), these cobalt complexes exhibited high catalytic activity and *cis*-1,4-selectivity toward 1,3-butadiene polymerization. The selectivity of the catalytic system could be switched from *cis*-1,4 to 1,2-fashion via the addition of PPh_3 . The effects of ligand environment, polymerization temperature, and $[\text{Al}]/[\text{Co}]$ ratio on the polymerization were investigated in detail.

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1. Introduction

The development of new catalysts for the chemo- and stereo-selective polymerization of conjugated dienes has attracted considerable attention in the past decades [1–5]. Numerous catalyst systems based on transition metals (Ti, Ni, Co, etc.) and rare earth metal have been developed so far [6–8]. Among them, cobalt-based catalyst systems are of particular interest because they can produce polybutadienes with versatile microstructures including *cis*-1,4, *trans*-1,4, and syndiotactic-1,2 isomers depending on the catalyst formulation [9–11]. Additionally, the catalytic activity and selectivity of catalysts mainly depend on the steric and electronic nature of the active site. In recent years, research interest has been focused on the design and synthesis of well-defined single-site catalysts in order to gain precise control of the catalysis behavior and polymer composition [12–15]. Since the discovery of bis(arylimino)pyridine ligated Co(II) and iron(II) complexes as effective catalysts for ethylene polymerization/oligomerization [16,17], a variety of transition metal complexes bearing α -diimine, pyridinediimine, and their derivatives have been synthesized and exploited as catalyst precursors for olefin polymerization [18–24]. Tremendous progress has also been made in the aspect

of conjugated diene polymerization. For example, (salen)cobalt(II) [25] and bis(salicylaldimine) cobalt(II) [26] were reported to be highly active for *cis*-1,4 polymerization of 1,3-butadiene. Cobalt dichloride complexes bearing various tridentate ligands such as 2,6-bis(imino)pyridine [6,27], 2,6-bis(pyrazol)pyridine [28], bis(N-arylcaboximidoylchloride)pyridine [29], 2-arylimino-6-(alcohol) pyridine/2-arylamino-6-(alcohol) pyridine [30], and 3-aryliminomethyl-2-hydroxybenzaldehyde [31] afforded *cis*-1,4 polybutadienes in high yields.

Pyridine bisoxazoline (Pybox) is an important class of ligands in scientific research owing to its facile preparation and easy modification of the parent framework [32,33]. Various Pybox/metal complexes have been synthesized and found applications in asymmetrical catalysis. However, its potential as coordination polymerization catalyst is quite limited. Iron(II) [34] and ruthenium(II) [35] complexes bearing 2,6-bis[4'-(S)-isopropylloxazolin-2'-yl]pyridine were reported as catalytic precursors for ethylene polymerization but exhibited low activities. To our knowledge, there is only one paper that reported the polymerization of 1,3-butadiene with 2,6-bis[4'-(S)-isopropylloxazolin-2'-yl]pyridine chromium trichloride/MMAO catalyst [36]. On the other hand, many studies have disclosed that the ligand environment of the complex affected catalytic behaviors significantly. In the present study, a series of pyridine–oxazoline and quinoline–oxazoline ligated Co(II) complexes were synthesized and characterized. Furthermore, the effects of the ligand and polymerization

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parameter on the activity and selectivity toward 1,3-butadiene polymerization was investigated in detail.

2. Experimental part

2.1. General consideration

The molecular weights (M_n) and molecular weight distributions (MWD) of polymers 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 \times 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. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Varian Unity spectrometer in CDCl_3 or $\text{DMSO}-d_6$ at room temperature. IR spectra were recorded on a BRUKER Vertex-70 FT-IR spectrophotometer. Elemental analysis was performed on an elemental Vario EL spectrometer. The proportion of 1,2-, *cis*-1,4, and *trans*-1,4 units of polymer were determined by IR, ^1H -NMR, and ^{13}C -NMR spectra [37,38].

All the manipulations were performed under an atmosphere of dry argon by using standard Schlenk techniques or in a glove box. Toluene, tetrahydrofuran (THF), and diethyl ether were freshly obtained by distillation under nitrogen from sodium-benzophenone ketyl. CHCl_3 and triethylamine were refluxed over CaH_2 and distilled prior to use. *N,N*-dimethylformamide (DMF) was dried over CaH_2 and then distilled under reduced pressure before use. 1,3-Butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å molecule sieve and KOH prior to use. MAO (10 wt%) was purchased from Akzo Noble and used as received. Ethylaluminum sesquichloride (EASC) was purchased from Sigma–Aldrich Co. and diluted to 1.0 mol/L solution by toluene. Other chemicals were commercially available and used as received unless otherwise mentioned. The ligands were synthesized referring to the modified literature methods (Scheme 1) [32,39–41].

2.2. Synthesis and characterization of ligands **3a–e** and **5a–e**

2.2.1. Synthesis of 2-(oxazolin-2'-yl) pyridine, Pyox (**3a**)

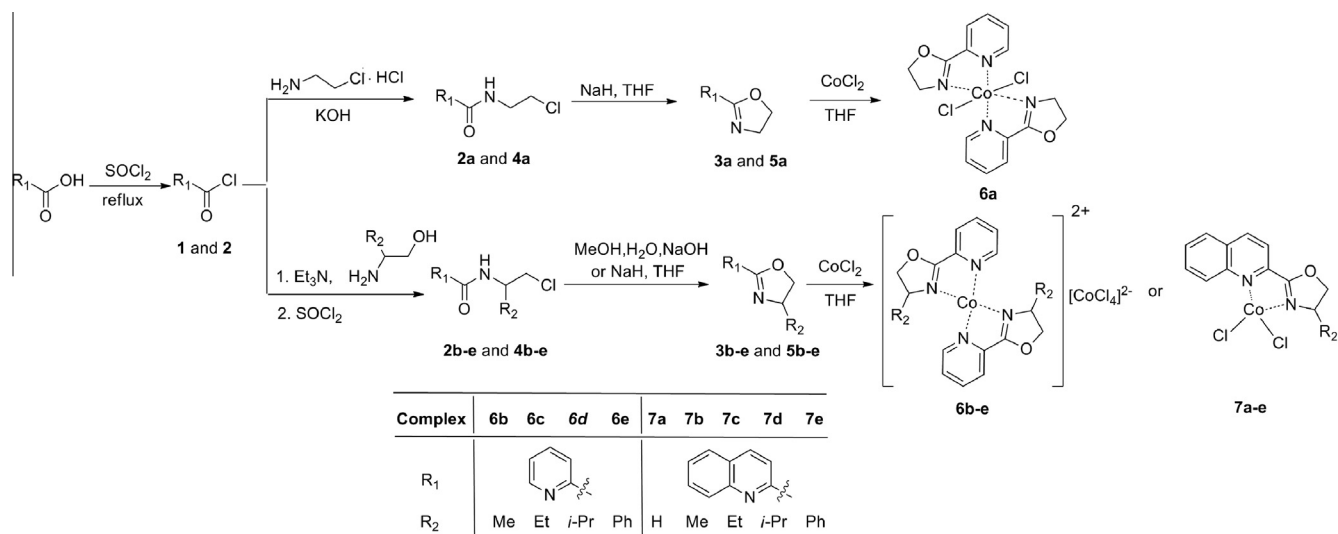
Pyridine-2-carboxylic acid (1.23 g, 10.0 mmol) was treated with SOCl_2 (15.0 mL) at reflux temperature under a nitrogen

atmosphere. Excess SOCl_2 was then removed under reduced pressure to give the acid chloride as a white solid (100%). The chloroform solution of crude 2-pyridine carbonyl chloride was slowly added to an aqueous solution of chloroethylamine hydrochloride (2.55 g, 22.0 mmol) and KOH (1.69 g, 30.0 mmol) at 0 °C. After 1 h, the aqueous layer was discarded, the organic layer filtered and washed with water. After the solvent was removed under reduced pressure, the crude carboxamide was yielded as a light yellow solid. This solid was dissolved in THF and then added to a suspension of NaH (0.60 g, 60% in mineral oil) in THF at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and then quenched with 10% HCl aq. The THF was removed under reduced pressure, and the residue was dissolved in dichloromethane. The resulting organic layer was dried over anhydrous MgSO_4 . After evaporating the solvent, the product was obtained as a white powder in 60% yield (0.89 g). ^1H NMR (CDCl_3 , ppm): 8.71 (d, $J = 4.5$ Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.79 (td, $J = 7.8$, 1.4 Hz, 1H), 7.46–7.35 (m, 1H), 4.53 (t, $J = 9.6$ Hz, 2H), 4.14 (t, $J = 9.7$ Hz, 2H). ^{13}C NMR (CDCl_3 , ppm): 163.93, 149.73, 146.95, 136.60, 125.49, 123.85, 68.23, 55.19. FT-IR (KBr; cm^{-1}): 1661, 1584, 1471, 1366, 1266, 1100, 940, 800, 748, 672. Anal. Calc. for $\text{C}_8\text{H}_8\text{N}_2\text{O}$ (148.16): C, 64.85; H, 5.44; N, 18.91. Found: C, 64.72; H, 5.59; N, 19.20%.

2.2.2. Synthesis of 2-[4'-(*S*)-methyloxazolin-2'-yl]pyridine, Me-Pyox (**3b**)

Crude 2-pyridine carbonyl chloride was prepared by the same method as for **3a**. The obtained crude carbonyl chloride reacted with (*S*)-2-Amino-1-propanol with triethylamine as a deacid reagent, then excess SOCl_2 was added, and the solution was reflux for 2 h. The resultant mixture was poured into ice water.

The organic layer was collected, washed with brine (20 mL \times 3) and aqueous K_2CO_3 aq. (0.1 mol/L, 30 mL), and dried over anhydrous MgSO_4 . After evaporating the solvent, the crude product was purified by silica gel column chromatography to give **2b** (1.59 g, ca. 8.0 mmol) as a light yellow solid. The solid (3.20 g) was treated with a THF suspension of NaH (0.60 g) at room temperature for 24 h. The THF was removed under reduced pressure, and the residue was dissolved in dichloromethane. The organic layer was dried over Na_2SO_4 . After evaporation the solvent, the product was obtained as a colorless liquid (1.04 g, 64% yield). ^1H NMR (CDCl_3 , ppm): 8.71 (d, $J = 4.4$ Hz, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.77 (td, $J = 7.8$, 1.3 Hz, 1H), 7.44–7.33 (m, 1H), 4.69–4.57



Scheme 1. Synthesis of complexes **6a–e** and **7a–e**.

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