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Trans-1,4 selective polymerization of 1,3-butadiene with symmetry pincer chromium complexes activated by MMAO

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ABSTRACT

Tridentate chromium complexes (**Cr1**–**Cr7**) incorporated with symmetrical pincer ligand bis(arylimino) pyridine and bis(pyrzaolyl)pyridine have been synthesized and characterized by elemental analyis, FT-IR as well as ESI-MS. X-ray diffraction reveals solids-state structures of **Cr2**, **Cr4** and **Cr6** all adopt pseudo-octahedral coordination environment with respect to metal center. All complexes have been tested in stereoregulated polymerization of butadiene under various polymerization conditions. The *trans*-1,4 and *cis*-1,4 enchainment of resultant polymer are found to be dependent on the structure of ligand and amount of activator used. Under the optimized condition, free *ortho*-substitutes Cr catalysts **Cr1**, **Cr3**, **Cr4** and **Cr6** are capable of initiating high *trans*-1,4 selectivity (*trans*-1,4: 89.2%–92.0%) with good polymer yields (71.5%–78.0%), while counterparts with *ortho*-positioned alkyl groups **Cr2**, **Cr5** and **Cr7** display mixed selectivities with moderate polymer yields. The sterical effect of ligand and amount of MMAO on the catalytic performance, in particular, the stereoselectivity and polymer yield, has been also elucidated by conjugated diene polymerization mechanism.

Introduction

The stereoselective polymerization of conjugated dienes promoted by transition and rare earth metal complexes is an extensively studied topic and challenging field in both academic and industrial environments for the relevance of these materials as synthetic rubbers. *Trans*-1,4 regulated polybutadiene has attracted renewed interest over the past decade, as such polymer possesses excellent dynamic properties, including excellent anti-fatigue properties, low rolling resistance, low heat buildup, good strength and low abrasion loss [1]. They can also be copolymerized with ethylene [2] and styrene [3] to afford high valued copolymers or be blended with elastomers to prepare materials with unique mechanical properties. Contrast to vast exploration of *cis*-1,4 and 1,2 selective catalysts, study on *trans*-1,4 selective catalysis are conspicuously less, which might be the fact that 1,3-conjugated dienes kinetically prefer η^4-*cis* to η^2-*trans* coordination to active metal center, ultimately leading to *cis*-1,4 and 1,2-stereoregulated growing polymer chain [4–6].

Early research on *trans*-1,4-polybutadiene dates back to the infancy of Ziegler–Natta type of transition metal recipes like titanium, vanadium halides activated by aluminum alkyls which produce mixtures of polymers containing variable amounts of *trans*-1,4-polybutadiene depending on type of halogen [5]. Rare-earth metal compounds such as lanthanocene aluminates [7,8], lanthanide bis(allyl)s [9], lanthanide dialkyl [10–12] and neodymium alkoxides or aryl oxides [13,14] which need activation of borates or organo magnesium and aluminum, have been known for catalyzing *trans*-1,4 homo- and copolymerization of butadiene. Over the past decade, efforts to expand variety of ligand families for homogeneous catalysts able to polymerize butadiene have resulted in cascade exploration of *trans*-1,4 selective systems, notably, those based on various tridentated ligands for supporting Fe, V, Ti, and Cr complexes. The tridentate *N*,*N*,*N*-donor ligands (Chart 1) such as

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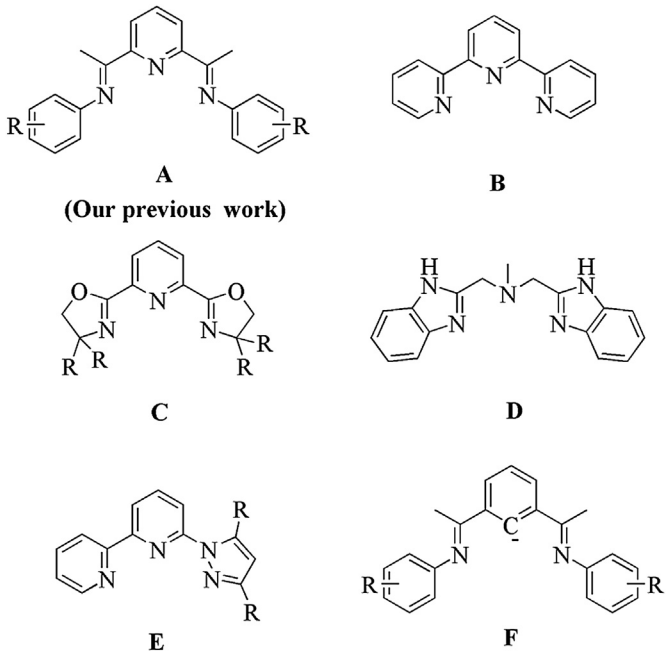


Chart 1. The reported tridentated *N,N,N* pincer ligand in butadiene polymerization.

2,6-bisiminopyridine [15–17], terpyridine [18], 2,6-bis(oxazoline) pyridine [19], bis(benzimidazolyl)amine [20–23] and 2-pyrazol-1,10-phenroline [24] have been well described for promoting good *trans*-1,4 selectivity. This may be related to the multi-dentate coordination ability of ligands, which are known for their special capability not only of stabilizing active species but inducing η^2-*trans* coordination of incoming monomer to metal center [4], however, the reason why this kind of ligand set can promote such unique *trans*-1,4 selectivity remains to be elucidated. Recently, a new type of titanium catalyst precursors incorporated with a chelated ligand (OSSO) having two phenolate units linked through a 1,ω-dithiaalkanediyl bridge $S(CH_2)_nS$ (n = 2 and 3) efficiently catalyze *trans*-1,4 homo-polymerization and copolymerization with styrene and ethylene, giving copolymers with unprecedented microstructural architectures [2,3].

The development of single-site Cr catalysts has also renewed interest for exploring stereoselective 1,3-conjugated diene catalysts. Collectively, the selectivity of homogeneous chromium catalysts is closely related to catalyst formula, in particular, the ligand framework and nature of dentated atoms, for example, chromiumdichloride compounds supported by bidentated phosphines ligands linked with alkyl chain (P,P-ligand) have been demonstrated as a syndio-1,2-selective catalyst [25,26]. Gibson and coworkers [21,22] explored bis(benzimidazolyl)amine (*N,N,N*-ligand) as an auxiliary ligand for chromium(III) trichloride, which results in a high active and *trans*-1,4 selective (99%) catalyst when activated with MMAO. The tridentated terpyridine (*N,N,N*) [27] and 1,3-bisiminobenzene (NCN) ligand incorporated complexes developed by Nakayama [28] and Mu [29], respectively, are also able to initiate *trans*-1,4 selective polymerization of butadiene with good activity. Despite various efficient catalysts have been explored, the ligand effect on catalytic performance have not yet been well understood, in particular, how the stereoselectivity is induced as well as the high activity is promoted by the ligand backbone and it's substitute has not yet been elucidated.

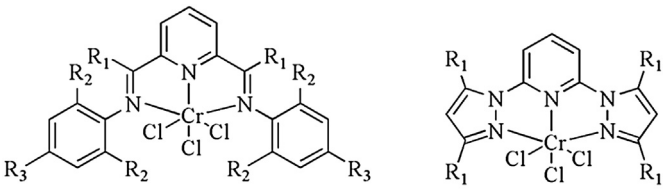
In the previous work, we described the metal dependent polymerization behaviors of 2,6-bis[(iminophenyl)methyl]pyridine chelated transition metal (Cr, Fe, Co and Ni) and found chromium, iron and cobalt complexes are *trans*-1,4 catalysis in polymerization of butadiene under proper conditions [17,30,31]. As continued work, herein, we focus on bisiminopyridine and bis(pyrazolyl) pyridine as auxiliary ligand for chromium complexes in selective polymerization of butadiene. The polymerization conditions and ligand structure effects, particularly, the ligand framework and the incorporated substitutes, on the selectivity and activity will be discussed by conjugated diene polymerization mechanism, and this might give hint on designing desirable catalyst.

Results and discussion

Syntheses and characterization and complexes

Ligands and the corresponding complexes were prepared in moderate to good yields via various modified procedures [17,32]. The reaction of $CrCl_3(THF)_3$ with 1.0 equiv. of the appropriate ligand in THF at room temperature under argon atmosphere afforded the corresponding complexes **Cr1**–**Cr7** (Chart 2), which were isolated as stable green solids. All products have been confirmed by FT-IR, elemental analysis and mass spectroscopy. In addition, single crystals of **Cr2**, **Cr4** and **Cr6** were obtained by slowly diffusion of ethyl ether to their corresponding methanol solution at room temperature, and their solid structures were further studied by single crystal X-ray diffraction. The crystal data and structure refinements were compiled in Table 1.

Single-crystal X-ray analysis reveals that complexes **Cr2** (Fig. 1), **Cr4** (Fig. 2), and **Cr6** (Fig. 3) all adopt a distort octahedral geometry in a meridional manner with metal center chelated by tridentate ligand through two nitrogen atoms and a pyridine nitrogen atom, where the equatorial plane consists of theses three nitrogen atoms, and one chlorine atom. The complexes **Cr2** and **Cr4** display approximate C_s symmetry about a plane consisted of three chlorine groups and the pyridyl nitrogen atom, while **Cr6** has C_2 symmetry. The equatorial planes of **Cr2** and **Cr4** form dihedron angles of 65.67°, 77.18° (for **Cr2**) and 81.08°, 67.67° (for **Cr4**) with two pyridine rings, while equatorial plane is almost coplanar to two pyrazoles in **Cr6**. The bond distance of Cr–N (pyridine) in all three complexes are longer than those of Cr–N(imino, pyrazole), with Cr–N (pyridine) length decreasing in the order of **Cr6** > **Cr2** > **Cr4**. The unsymmetrical Cr–N(imino, pyrazole) bond are also varied with the ligand type and substitutes, following the decreasing trend of **Cr2** > **Cr4** > **Cr6**. The bond distance between Cr atom and *trans*-positioned chloride are longer than those of Cr–Cl (*cis*-positioned), suggesting that subtle inequality of three chlorides. The N1–Cr–N3 angle in complex **Cr2** is 151.69(13)°, slightly smaller than 154.4(2)° and 153.92(6)° found in the corresponding **Cr4** and



Cr1, $R_1 = R_2 = R_3 = H$;
Cr2, $R_1 = H$, $R_2 = {}^iPr$, $R_3 = H$;
Cr3, $R_1 = CH_3$, $R_2 = R_3 = H$;
Cr4, $R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$;
Cr5, $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$.

Cr6, $R_1 = H$;
Cr7, $R_1 = CH_3$.

Chart 2. The structures of tridentated *N,N,N* pincer ligand ligated chromium complexes in this study.