Contents lists available at SciVerse ScienceDirect



Journal of Organometallic Chemistry



Stereospecific polymerization of 1,3-butadiene catalyzed by cobalt complexes bearing *N*-containing diphosphine PNP ligands

Lin Chen^a, Pengfei Ai^a, Jianming Gu^b, Suyun Jie^{a,*}, Bo-Geng Li^{a,*}

^a State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
^b Department of Chemistry, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history: Received 20 April 2012 Received in revised form 24 May 2012 Accepted 30 May 2012

Keywords: Cobalt Phosphine 1,3-Butadiene Polymerization

1. Introduction

It is well known that the polymerization of 1,3-butadiene (BD) leads to the formation of polybutadienes (PBDs) with different microstructures, including cis-1,4-, trans-1,4-, syndiotactic 1,2- and isotactic 1,2-PBD via 1,4- or 1,2-insertions, which endow PBDs with extensive and diverse properties and applications [1]. For the industrial production of PBDs, the Ziegler-Natta catalysts based on titanium [2], nickel [3,4], cobalt [5,6] or neodymium [7] with halides, carboxylates, acetylacetonates or alcoholates, are currently employed in combination with various organoaluminums. Among those catalysts, the addition of phosphines to certain cobalt-based catalytic systems could alter the regio- and/or stereospecificity of the active species from cis-1,4-specific to syndiotactic 1,2-specific [8–17]. For example, the halides and carboxylates of cobalt are stereoselective to high cis-1,4-PBD upon activation with methylaluminoxane (MAO) [18-22]. However, the cobalt phosphine complexes of the type $CoCl_2(PRPh_2)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, and cyclohexyl) have been reported to be highly active and stereoselective in the polymerization of butadiene in combination with MAO, giving 1,2-vinyl polymers (1,2-vinyl content: ca. 80%) with a syndiotacticity degree depending on the phosphine ligand bound to the metal center [10–17].

In the interest of better control over catalytic activity, molecular weight and microstructure of the resulting polymers, well-defined

ABSTRACT

A series of cobalt complexes bearing *N*-containing diphosphine PNP ligands has been synthesized and characterized. The nature of the ligand structure affects the binding of the ligand to the cobalt center and determines the coordination geometry of the cobalt complexes. All the complexes have been employed to catalyze the polymerization of 1,3-butadiene, in combination with methylaluminoxane (MAO) or ethylaluminum sesquichloride (EASC) as the cocatalyst. Both the nature of the ligand and the type of cocatalyst had a remarkable influence on the polymerization activity, microstructure and molecular weight of the resulting polymers. The [Co]/MAO catalytic systems resulted in relatively lower conversions of butadiene and *cis*-1,4 contents in the polymers than the corresponding [Co]/EASC catalytic systems. Upon activation with EASC, the polymerization behaviors of the catalytic systems were also affected by the reaction parameters.

© 2012 Elsevier B.V. All rights reserved.

organometallic single-site catalysts bearing chelating organic ligands, mainly based on rare earth metals and first-row transition metals, have been focused on [1,23-27]. Among those cobalt-based catalysts, the addition of triphenylphosphine to the chelate cobalt catalytic systems containing bis(benzimidazolyl)amine ligands led to great increase in the 1,2-vinyl content, when activated with MAO [28,29]. However, the addition of triphenylphosphine to the catalytic systems consisting of cobalt complexes with 3aryliminomethyl-2-hydroxybenzaldehyde ligands and ethylaluminum sesquichloride (EASC) didn't change the polymer microstructure [30]. This demonstrated that the type of cocatalyt affected importantly not only the catalytic activity but also the microstructure of polymers whether the phosphine-containing or phosphine-free catalytic systems. In order to further prove this point, a series of chelate cobalt complexes bearing nitrogencontaining phosphine PNP ligands, which combine two soft (P) and one hard (N) donor atoms to give flexible coordination modes, has been synthesized and investigated in the polymerization of butadiene with the cocatalyst MAO or EASC in this paper.

2. Results and discussion

2.1. Synthesis and characterization of PNP ligands and their cobalt complexes

Bis[2-(diphenylphosphino)ethyl]amine (**L1**, PNHP) was prepared as an air-stable bis[2-(diphenylphosphino)ethyl]amine hydrochloride (**L1**·HCl, PNHP·HCl) by the reaction of bis(2-

^{*} Corresponding authors. Tel.: +86 571 87951515; fax: +86 571 87951612. *E-mail addresses:* jiesy@zju.edu.cn (S. Jie), bgli@zju.edu.cn (B.-G. Li).

⁰⁰²²⁻³²⁸X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.05.051

chloroethyl)amine hydrochloride with the in-situ formed potassium diphenylphosphide from diphenylphosphine and potassium tert-butoxide in dry THF according to the literature method [31–33]. This ligand is a typical representative of N-containing diphosphine PNP ligands where an amine nitrogen atom is doubly connected via highly flexible ethylenic chains to two diphenylphosphine ends. The ligand **L1** · HCl reacted directly with one equiv. of CoCl₂ in degassed absolute ethanol at room temperature to vield a green powder, which was confirmed to be complex **1a** by the single crystal X-ray diffraction analysis (Fig. 1). However, the reaction of ligand L1, obtained by the treatment of L1 · HCl with sodium hydroxide, with one equiv. of CoCl₂ under the same conditions afforded the corresponding complex 1b as a purple powder (Scheme 1). Although it was not successful to grow crystals suitable for a crystallographic analysis, we assigned **1b** to be a tetrahedral geometry with the cobalt center coordinated by two chlorides and the two phosphorus atoms from the ligand, as reported in the literature [34]. This ligand was usually used to form chromium complexes as the efficient catalyst precursors for the selective trimerization of ethylene [35-37] and its nickel and palladium complexes have been also reported [33,38,39]. Since the complexes **1a** and **1b** have low solubility in ethanol, the products directly precipitated from the reaction solutions, which made for convenient separation and good yields.

In the solid state of complex 1a, one chloride of HCl molecule from the ligand PNHP·HCl is unexpectedly coordinated to the cobalt center, which makes the formation of six-coordinated complex displaying a distorted octahedral geometry as shown in Fig. 1. It has been reported that the addition of a third chloride. from either hydrochloric acid or ammonium chloride, to tetrahedral cobalt(II) complex with an aminodiphosphine ligand, resulted in the transfer of the third chloride to the cobalt center, even if the coordination geometry around the cobalt center was still tetrahedronal with PNP acting as a monodentate ligand through one phosphorus atom [40]. In the molecular structure of 1a, PNP atoms of the tridentate ligand are coordinated in a meridional manner, in which the P1, P2, Cl1, and Cl3 atoms could be located in an equatorial plane and the axial bonds nearly form a straight angle (N1-Co1-Cl2, 179.1(2)°). All the bond angles in the equatorial plane are very close to a right angle in the range from 88.24(1)° to 90.74(1)°. The Co1–N1 bond length (1.997(7) Å) is short enough to form a strong coordination bond. The Co1-Cl1 (from HCl) bond was slightly shorter than the Co1–Cl2 and Co1–Cl3 (both from CoCl₂) bonds. The slight difference of the two Co-P bonds indicates the asymmetry of the whole molecule without a mirror plane.

2,6-Bis(chloromethyl)pyridine was prepared by the quantitative transformation of 2,6-bis(hydroxymethyl)pyridine reacted with the stoichiometric quantity of thionyl chloride in dry THF [41]. The



CI3





Scheme 1. Synthesis of complexes 1a and 1b.

reaction of 2,6-bis(chloromethyl)pyridine and the in-situ formed potassium diphenylphosphide from diphenylphosphine and potassium *tert*-butoxide in dry THF afforded the formation of 2,6-bis((diphenylphosphino)methyl)pyridine (**L2**) in good yield, in which the PPh₂ substituents are connected to the central pyridine backbone by CH₂ groups. Complex **2** was readily prepared as a greenish blue powder by the reaction of ligand **L2** with CoCl₂ in absolute ethanol (Scheme 2), forming a trigonal-bipyramidal coordination geometry with two 5-membered chelate rings, which was applied as catalyst precursors for the polymerization of ethylene after activation with MAO [42], but much less active than the bis(imino)pyridyl catalysts (NNN ligands) [43,44].

The Schiff-base condensation 2reaction of diphenylphosphinobenzenaldehyde with 2-(2-PCHO)aminophenyldiphenylphosphine (2-PNH₂) in the presence of a catalytic amount of toluene-p-sulfonic acid in refluxing benzene yielded the ligand, 2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene]aniline (L3, PN=CHP) (Scheme 3), which has been used for binding to a range of metals [45–47]. The reduction of C=N double bond in the ligand L3 with the excess amount of sodium borohydride in methanol resulted in the formation of ligand L4 with amino group. These two ligands can be visualized as two triphenylphosphine moieties tethered together in the ortho positions by an imino or amino linker. The corresponding cobalt complex **3** and **4** with this type of ligands acting as a bidentate ligand through two phosphorus atoms binding to the cobalt center were obtained as blue or green powders. Complex 3 was reported with less interest for ethylene activity because of its inactivity on treatment with Al-containing cocatalyst (MAO or AlEt₃) [48]. All the synthesized cobalt complexes are air-stable in the solid state, but in solution they are sensitive to traces of water and oxygen.

2.2. Butadiene polymerization catalyzed by cobalt complexes

2.2.1. MAO as cocatalyst

The CoCl₂(PR¹R²₂)₂/MAO (R¹, R² = Me, Et, n-Pr, i-Pr, t-Bu, Cy, Ph) and CoCl₂[R₂P(CH₂)_nPR₂]/MAO (R = Me, Et, Ph; n = 1,2) catalytic



Scheme 2. Synthesis of ligand L2 and complex 2.



Scheme 3. Synthesis of ligands L3, L4 and complexes 3, 4.

systems were reported to be very active for the polymerization of butadiene [25]; the former yielded the mixture of cis-1,4-PBD and 1,2-PBD depending on the bulkiness of R¹ and R² groups on the phosphorous atom, whereas the latter bearing bidentate PP ligands mainly produced *cis*-1,4-PBD with the *cis*-1,4 content over 94% [49]. Therefore, the solution polymerizations of butadiene catalyzed by complexes 1a, 1b, and 2–4 bearing N-containing diphosphine PNP ligands $[CoCl_2(PPh_3)_2(5)]$ as a reference catalyst were firstly carried out upon activation with MAO and the results are shown in Table 1. The chelate complexes 1a, 1b, and 2–4/MAO systems were found to be much less active than complex 5 with free PPh₃ ligands and the corresponding conversions of butadiene ranged from 12.7% to 46.1%, while the conversion of 5/MAO system reached 94.2% under the same reaction conditions. This indicated that the chelate catalyst structures were more unfavorable than the nonchelate ones for the current PNP cobalt complexes/MAO catalytic systems in butadiene polymerization. It is interesting to notice that much higher conversion of butadiene was obtained when the imino group in ligand L3 was reduced to amino group (ligand L4), comparing complex **3** (conversion: 12.7%) with complex **4** (conversion: 46.1%) although the nitrogen atoms were not coordinated to the cobalt center (entries 4 and 5 in Table 1). Similar to the results reported in the literature [16,17], the 5/MAO system produced much more amount of 1,2-PBD (1,2-vinyl content: 76.9%) than cis-1,4-PBD (cis-1,4 content: 20.6%) because the nature of PPh₃ as a strong σ -donor makes it more preferable to gain a high content of 1,2-PBD (entry 6 in Table 1). However, for the chelate complexes 1a, 1b, and 2-4/MAO systems, the *cis*-1,4-PBD as the main product ranging from 75.7% to 88.8% was obtained along with a relatively higher content (9.0%-20.6%) of 1,2-PBD formed. Furthermore, among the above cobalt complexes with PNP ligands, the four-coordinated 1b, 3 and 4 yielded slightly lower cis-1,4 and higher 1,2 contents than the other five or six-coordinated 1a and 2. The PBDs produced by all the

| Table 1 |
|--|
| Polymerization of 1,3-butadiene with complexes 1a, 1b, 2–5/MAO. ^a |

| Entry | Cat. | Conv. (%) | M_n^{b} (10 ⁴ g/mol) | M_w/M_n^b | Microstructure ^c (mol%) | | |
|-------|------|-----------|-----------------------------------|-------------|------------------------------------|------------|------|
| | | | | | cis-1,4- | trans-1,4- | 1,2- |
| 1 | 1a | 18.7 | 12.7 | 2.37 | 83.1 | 2.8 | 14.1 |
| 2 | 1b | 25.4 | 10.4 | 2.76 | 80.3 | 2.8 | 16.9 |
| 3 | 2 | 17.7 | 9.04 | 2.35 | 88.8 | 2.2 | 9.0 |
| 4 | 3 | 12.7 | 12.7 | 2.45 | 75.7 | 3.7 | 20.6 |
| 5 | 4 | 46.1 | 9.94 | 2.78 | 78.9 | 1.8 | 19.3 |
| 6 | 5 | 94.2 | 8.20 | 3.57 | 20.6 | 2.5 | 76.9 |

 a Polymerization conditions: precatalyst: 5.0 μ mol, cocat.: MAO, [Al]/[Co]: 1000, solvent: toluene, total volume: 10 mL, [BD]/[Co]: 2000, reaction temperature: 25 °C, reaction time: 2 h.

^b Determined by GPC against polystyrene standards and reported uncorrected.

^c Determined by ¹H and ¹³C NMR spectroscopy.

complexes had moderate molecular weight (82,000–127,000 g/ mol) with relatively narrow molecular weight distributions (2.35–3.57) and the lowest molecular weight along with the broadest molecular weight distribution was observed for complex **5** (entry 6 in Table 1).

2.2.2. EASC as cocatalyst

In order to gain higher catalytic activities and *cis*-1.4 content. ethylaluminum sesquichloride (EASC) was attempted as cocatalyst since it has been proved to be more effective for the chelate cobalt complexes in the polymerization of butadiene [30,50-54]. With the 1a/EASC catalytic system, reaction parameters were varied to investigate their effects on the catalytic activities and properties of the resulting polymers and to optimize the polymerization conditions. The Al/Co molar ratio had a significant influence on the catalytic activity and molecular weight. The Al/Co molar ratio of 20 afforded the 60.1% conversion of butadiene (entry 1 in Table 2). The conversion of butadiene and molecular weight of the resulting polymers increased gradually along with the increase of Al/Co molar ratio from 20 to 80 (entries 1-3 in Table 2) and a complete conversion of butadiene was obtained under the Al/Co molar ratio of 80 in 1 h. When the Al/Co molar ratio was further increased to 160, the monomer could be completely transformed to polymer as well, but the molecular weight of obtained polymer decreased obviously, from which we could infer that the chain transfer to aluminum reacted on the molecular weight in the current catalytic system. However, the Al/Co molar ratio slightly affected the molecular weight distribution in the range of 2.09-2.57 and the microstructure of the resulting polymers didn't change apparently, having the *cis*-1,4 content in the range of 95.6%–96.7% along with small amounts of trans-1,4-PBD (1.2%-2.6%) and 1,2-PBD (1.8%-2.5%).

The butadiene polymerizations were also carried out over the temperature range from 0 to 90 °C at an Al/Co molar ratio of 80 with the 1a/EASC catalytic system (entries 3 and 5-8 in Table 2). Similar to other chelate cobalt-based catalysts [30,50–53], the butadiene polymerization behavior with the **1a**/EASC catalytic system was very sensitive to reaction temperature (Figs. 2 and 3). The 29.0% conversion of butadiene, highest cis-1,4 content of 98.6% and highest molecular weight were obtained at 0 °C. The highest catalytic activity was gained at 25 °C with the complete conversion of butadiene. However, the catalytic activity decreased remarkably as the temperature was enhanced. The 1a/EASC catalytic system was relatively stable at 50 °C and the conversion of butadiene was 85.2%. But the conversion dropped sharply to 48.2% at 70 °C and 20.1% at 90 °C, which was in consistent with the olefin polymerization catalyzed by the late-transition metal complexes and was generally explained due to the deactivation of active species at higher temperatures [55–57]. In general, the variation of reaction temperature results in the important change of polymer microstructure. The content of cis-1,4-PBDs in the polymers decreased gradually along with the elevation of reaction temperature, but the trend of trans-1,4 content was opposite. When the temperature was increased from 0 °C to 70 °C, the cis-1,4 content in the polymers decreased from 98.6% to 92.0%. Nevertheless, for the current system, the PBDs produced at 50 °C and 70 °C had similar molecular weights and microstructures (Figs. 2 and 3). The polymerization at 90 °C yielded the 13.8% content of trans-1,4 isomer and the 9.4% content of 1,2 isomer; and the cis-1,4 content reduced to 76.8%. The molecular weights of PBDs were also decreased from 283,000 to 23,000 g/mol as the temperature was increased from 0 °C to 90 °C, but the molecular weight distributions (1.65-2.27) of PBDs didn't change greatly.

The other synthesized cobalt complexes (**1b** and **2–5**) were also used for butadiene polymerization to examine the influence of ligand environment on catalytic activity and properties of the

| Table 2 |
|---|
| Polymerization of 1,3-butadiene with complexes 1a, 1b, 2–5/EASC. ^a |

| Entry | Cat. | Al/Co | Т | t | Conv. | M_n^b | $M_{\rm w}/M_{\rm n}{}^{\rm b}$ | Microstructure ^c (mol%) | | |
|-------|------|-------|------|-------|-------|-------------------------|---------------------------------|------------------------------------|------------|------|
| | | | (°C) | (min) | (%) | (10 ⁵ g/mol) | | cis-1,4- | trans-1,4- | 1,2- |
| 1 | 1a | 20 | 25 | 60 | 60.1 | 1.76 | 2.09 | 96.2 | 1.3 | 2.5 |
| 2 | 1a | 40 | 25 | 60 | 83.6 | 2.12 | 2.27 | 96.7 | 1.3 | 2.0 |
| 3 | 1a | 80 | 25 | 60 | 100 | 2.32 | 2.27 | 96.6 | 1.2 | 2.2 |
| 4 | 1a | 160 | 25 | 60 | 100 | 1.60 | 2.57 | 95.6 | 2.6 | 1.8 |
| 5 | 1a | 80 | 0 | 60 | 29.0 | 2.8s | 1.65 | 98.6 | 0 | 1.4 |
| 6 | 1a | 80 | 50 | 60 | 85.2 | 0.90 | 2.33 | 93.1 | 3.7 | 3.2 |
| 7 | 1a | 80 | 70 | 60 | 48.2 | 0.83 | 1.90 | 92.0 | 4.7 | 3.3 |
| 8 | 1a | 80 | 90 | 60 | 20.1 | 0.23 | 1.70 | 76.8 | 13.8 | 9.4 |
| 9 | 1b | 80 | 25 | 60 | 95.3 | 2.33 | 2.19 | 96.6 | 1.1 | 2.3 |
| 10 | 2 | 80 | 25 | 60 | 100 | 1.91 | 2.34 | 97.1 | 1.4 | 1.5 |
| 11 | 3 | 80 | 25 | 60 | 34.5 | 3.90 | 1.84 | 98.4 | 0 | 1.6 |
| 12 | 4 | 80 | 25 | 60 | 100 | 2.40 | 2.29 | 98.1 | 0 | 1.9 |
| 13 | 5 | 80 | 25 | 60 | 100 | 2.15 | 2.24 | 96.9 | 1.4 | 1.7 |
| 14 | 1a | 80 | 25 | 30 | 98.0 | 1.81 | 2.68 | 97.3 | 0.9 | 1.8 |
| 15 | 1b | 80 | 25 | 30 | 67.0 | 2.33 | 2.12 | 97.0 | 0.7 | 2.3 |
| 16 | 2 | 80 | 25 | 30 | 92.3 | 1.89 | 2.39 | 98.0 | 0.5 | 1.5 |
| 17 | 3 | 80 | 25 | 30 | 22.7 | 2.89 | 1.99 | 98.1 | 0 | 1.9 |
| 18 | 4 | 80 | 25 | 30 | 92.5 | 2.30 | 1.94 | 98.7 | 0 | 1.3 |
| 19 | 5 | 80 | 25 | 30 | 100 | 1.76 | 2.05 | 96.9 | 1.3 | 1.8 |

^a Polymerization conditions: precatalyst: 5.0 µmol, cocat.: EASC, solvent: toluene, total volume: 10 mL, [BD]/[Co]: 2000.

^b Determined by GPC against polystyrene standards and reported uncorrected.

^c Determined by ¹H and ¹³C NMR spectroscopy.

resulting polymers. The complete conversions of butadiene were obtained by the 1a, 2, 4, 5/EASC catalytic systems and the 1b/EASC system gave a slightly lower conversion of butadiene (95.3%, entry 9 in Table 2). However, complex 3 with imino group was much less active for butadiene polymerization and the 34.5% conversion of butadiene was acquired under the same conditions (entry 11 in Table 2). In contrast with the [Co]/MAO catalytic systems, the PBDs produced by all the [Co]/EASC catalytic systems had high cis-1,4 contents (96.6%-98.4%) and higher molecular weight (191,000–390,000 g/mol). The formation of high *cis*-1,4-PBD with the $CoCl_2(PPh_3)_2$ (5)/EASC system proved that the addition of PPh₃ to the P-free [Co]/EASC could not change the microstructure of PBDs or further increase the 1,2-vinyl content [30]. In order to make a better comparison, the reaction time was shortened from 1 h to 30 min. The high conversions of butadiene (92.3%–100%) were still maintained by the 1a, 2, 4, 5/EASC catalytic systems in 30 min, while the conspicuous decrease in monomer conversion was observed with the 1b, 3/EASC catalytic systems, to 67.0% and 22.7% in 30 min, respectively. Differently from the MAO systems, the sixcoordinated complex 1a (98.0% in 30 min) produced a higher conversion of butadiene than the corresponding four-coordinated 1b (67.0% in 30 min) upon activation with EASC as cocatalyst. The complex 4 with amino group in the ligand was much more active for butadiene polymerization than the complex **3** with imino group in either 1 h or 30 min, which probably ascribed to the rigid ligand structure and bulkiness of L3 restricting the insertion of butadiene to the active center in more extent. The molecular weights of PBDs obtained in 30 min were slightly lower than the corresponding ones in 1 h. However, the variation of reaction time nearly didn't affect the molecular weight distributions (1.94-2.68) and the microstructures (cis-1,4 contents in the range of 96.9%-98.7%) of the resulting polymers.



Fig. 2. The effects of reaction temperature on the conversion (%) of butadiene (\blacksquare) and molecular weight of PBDs (\blacktriangleleft) with the **1a**/EASC catalytic system (entries 3 and 5–8 in Table 2).



Fig. 3. Microstructure (%) of PBDs produced by the 1a/EASC catalytic system at different temperatures (entries 3 and 5–8 in Table 2).

Table 3

Crystallographic data and refinement parameters for complex 1a. 3CH₂Cl₂.

| Farmerela | C II CL CAND | D_{1} (Ma m ⁻³) | 1 440 |
|--------------------------|--------------------------|--|-------------------------------------|
| Formula | $C_{31}H_{36}Cl_9C0NP_2$ | D_{calc} (Nig m ⁻³) | 1.449 |
| Formula weight | 862.53 | $\mu ({\rm mm^{-1}})$ | 1.146 |
| Temp. (K) | 293(2) | F(000) | 1756 |
| Wavelength (Å) | 0.71073 | Crystal size(mm) | $0.48 \times 0.30 \times 0.28$ |
| Crystal system | Monoclinic | θ range (°) | 2.99-25.20 |
| Space group | P2(1)/c | Limiting indices | $-14 \le h \le 13, -20$ |
| | | | $\leq k \leq$ 20, $-25 \ l \leq$ 23 |
| a (Å) | 12.1774(8) | No. of rflns collected | 28,962 |
| b (Å) | 16.9996(10) | No. of unique rflns | 7095 |
| c (Å) | 19.5028(14) | No. of obsd | 2523 |
| | | $rflns(I > 2\sigma(I))$ | |
| α (°) | 90.00 | Completeness to θ (%) | 99.6 ($\theta = 25.20^{\circ}$) |
| β (°) | 101.621(3) | No. of parameters | 372 |
| γ (°) | 90.00 | Goodness-of-fit on F^2 | 0.943 |
| Volume (Å ³) | 3954.5(4) | Final R indices | $R_1 = 0.0939$, |
| | | $[I > 2\sigma(I)]$ | $wR_2 = 0.2374$ |
| Ζ | 4 | Largest diff peak, | 0.600, -0.449 |
| | | hole (e Å ⁻³) | |

3. Conclusions

In summary, a series of chelate cobalt complexes bearing Ncontaining diphosphine PNP ligands was synthesized and characterized. The cocatalyst EASC was more effective than MAO for the current cobalt-based catalytic systems to catalyze the polymerization of butadiene to give high cis-1,4-polybutadiene with high selectivity (>96.6%) (even for complex 5, CoCl₂(PPh₃)₂). Upon activation with EASC, the increase of Al/Co molar ratio enhanced the catalytic activity, but didn't change the polymer microstructure. The elevation of reaction temperature led to the decrease in the conversion of butadiene, cis-1,4 content and molecular weight. In combination with MAO, the resultant polymers had relatively higher 1,2-vinyl content (9.0%-20.6%). Among all the synthesized cobalt complexes, complex 3 with imino group in the ligand showed the lowest catalytic activity for both MAO and EASC systems. One conclusion could be drawn that both the type of cocatalyst and the nature of the ligand had an important influence on the catalytic activity and polymer microstructure for the current *N*-containing PNP cobalt-based catalysts.

4. Experimental section

4.1. General considerations and materials

All manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk techniques. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrometer by using KBr disks or liquid films for polybutadienes in the range 4000–400 cm⁻¹ ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker DMX-400 instrument in CDCl₃ with TMS as the internal standard. Elemental analysis was performed on a Flash EA1112 microanalyzer. The molecular weight and molecular weight distribution of polybutadienes were measured by GPC using Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards.

Toluene and tetrahydrofuran were refluxed over sodiumbenzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 10 wt% solution in toluene) was purchased from Akzo Nobel Corp. Ethylaluminum sesquichoride (0.4 M in hexane) was purchased from Acros Chemicals and used directly without further purification. Polymerization grade butadiene was purified by passing it through columns of KOH and molecular sieves. All other chemicals were obtained commercially and used without further purification unless otherwise stated. 2-(diphenylphosphino)benzaldehyde (2-PCHO) [58], 2-aminophenyldiphenylphosphine (2-PNH₂) [59], 2,6-bis((diphenylphosphino)methyl)pyridine (**L2**) and its cobalt complex (**2**) [42], and CoCl₂(PPh₃)₂ (**5**) [11,12] were prepared according to the literature.

4.2. Synthesis of ligands (L1, L3, L4)

4.2.1. Bis[2-(diphenylphosphino)ethyl]amine (L1)

Bis[2-(diphenylphosphino)ethyl]amine (**L1**, PNHP) was prepared as an air-stable bis[2-(diphenylphosphino)ethyl]amine hydrochloride (**L1**·HCl, PNHP·HCl) by the reaction of bis(2chloroethyl)amine hydrochloride with the in-situ formed potassium diphenylphosphide from diphenylphosphine and potassium *tert*-butoxide in dry THF according to a literature method [31–33]. FT-IR (KBr disc, cm⁻¹): 3422 (v_{N-H}), 1585, 1480, 1433, 1388, 748, 738, 695, 513. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.95 (s, 2 H, NH₂Cl), 7.38–7.28 (m, 20 H, Ph–H), 2.93–2.91 (m, 4 H, CH₂P), 2.54–2.50 (m, 4 H, NCH₂). ³¹P {¹H} NMR (CDCl₃), δ (ppm): –20.5 (s).

4.2.2. 2-(Diphenylphosphino)-N-[2-(diphenylphosphino)benzylide ne]benzenamine (L3)

The ligand **L3** (PN=CHP) was prepared by using a literature method [45]. FT-IR (KBr disc, cm⁻¹): 1625 (ν_{C} =_N), 1561, 1476, 1466, 1433, 1262, 1093, 1069, 1026, 803, 768, 740, 695, 503, 478. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.92 (d, 1 H, *J* = 4.2 Hz, CH=N), 7.97-7.94 (m, 1 H, Ar-H), 7.67-7.55 (m, 2 H, Ar-H), 7.50-7.47 (m, 1 H, Ar-H), 7.35-7.21 (m, 20 H, Ph-H), 7.06 (t, 1 H, *J* = 7.2 Hz, Ar-H), 6.82 (t, 1 H, Ar-H, *J* = 6.0 Hz), 6.75 (t, 1 H, Ar-H, *J* = 6.0 Hz), 6.46 (t, 1 H, Ar-H, *J* = 6.0 Hz).

4.2.3. 2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzyl] benzenamine (**L4**)

To a suspension of L3 (0.3169 g, 0.58 mmol) in 40 mL of anhydrous methanol was slowly added sodium borohydride (0.0655 g, 1.73 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The distilled water was added and methanol was removed under reduced pressure. The residual mixture was then extracted four times with dichloromethane, and the extracts were combined and dried over sodium sulfate. After filtration, CH₂Cl₂ was removed in vacuo and the residue was eluted on a silica column with petroleum ether and ethyl acetate (v:v = 5:1) to give L4 (PNHCH₂P) as a white solid (yield: 0.1632 g, 51.3%). FT-IR (KBr disc, cm⁻¹): 3422, 3053, 1589, 1484, 1436, 1176, 1119, 1097, 1069, 1027, 948, 745, 725, 694, 549, 517. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.35–7.27 (m, 20 H, Ph–H), 7.17–7.06 (m, 4 H, Ar-H), 6.81 (t, 1 H, J = 6.0 Hz, Ar-H), 6.74 (t, 1 H, I = 6.0 Hz, Ar-H), 6.57 (t, 1 H, I = 7.2 Hz, Ar-H), 6.33 (t, 1 H, I = 6.4 Hz, Ar-H), 4.46 (s, 2 H, CH₂NH). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 135.9 (d, ¹/₁ (PC) = 9.7), 135.5 (d, ¹/₁ (PC) = 7.4), 134.3, 134.1, 133.9. 133.8. 133.6. 132.9. 130.6. 129.0. 128.9. 128.8. 128.7. 128.6. 128.5, 127.0, 126.6, 126.5, 117.3, and 110.7 (aromatic-C), 46.0 (d, ³/ (PC) = 26.9, CH₂NH). ³¹P {¹H} NMR (CDCl₃), δ (ppm): -15.9 (s), -21.7 (s). Anal. Calcd for C₃₇H₃₁NP₂ (551.6): C, 80.57; H, 5.66; N, 2.54. Found: C, 80.74; H, 5.47; N, 2.25.

4.3. Preparation of cobalt(II) complexes

4.3.1. Preparation of CoCl₃(H)(PNHP) (1a)

The ligand, bis[2-(diphenylphosphino)ethyl]amine hydrochloride (L1·HCl) (0.2161 g, 0.45 mmol) and CoCl₂ (0.0570 g, 0.44 mmol) were added in a Schlenk flask that was purged three times with nitrogen and then charged with 20 mL of degassed anhydrous ethanol. The reaction mixture was stirred at room temperature for 3 h. The resulting mixture was concentrated and diethyl ether was added. Then the precipitate was filtered, washed with diethyl ether, and dried under vacuum to give cobalt complex **1a** as a green powder (yield: 0.2206 g, 82.7% based on cobalt). FT-IR (KBr disc, cm⁻¹): 3425, 3052, 2965, 1482, 1458, 1434, 1177, 1100, 998, 742, 695, 510. Anal. Calcd for $C_{28}H_{30}Cl_3CoNP_2$ (607.78): C, 55.33; H, 4.98; N, 2.30. Found: C, 55.29; H, 5.13; N, 2.30.

4.3.2. Preparation of CoCl₂(PNHP) (1b)

To a solution of bis[2-(diphenylphosphino)ethyllamine hydrochloride (L1·HCl) (0.1535 g, 0.32 mmol) in 20 mL of dichloromethane, a solution of NaOH (0.0178 g, 0.45 mmol) in 5 mL of ethanol was added. The mixture was stirred at room temperature for 1 h. The organic solvents were removed and the residue was extracted with CH₂Cl₂ to give bis[2-(diphenylphosphino)ethyl] amine (L1). The above ligand (L1) and CoCl₂ (0.0415 g, 0.32 mmol) were mixed in 20 mL of degassed anhydrous ethanol. The reaction mixture was stirred at room temperature for 3 h. The resulting mixture was concentrated and diethyl ether was added. Then the precipitate was filtered, washed with diethyl ether, and dried under vacuum to give cobalt complex 1b as a reddish violet powder (yield: 0.1367 g, 74.5% based on ligand). FT-IR (KBr disc, cm^{-1}): 3429, 3297, 3049, 2858, 1483, 1434, 1407, 1100, 1028, 1001, 841, 747, 695, 507. Anal. Calcd for C₂₈H₂₉Cl₂CoNP₂ (571.32): C, 58.86; H, 5.12; N, 2.45. Found: C, 59.22; H, 4.95; N, 2.49.

4.3.3. Preparation of CoCl₂(PN=CHP) (3)

Complex **3** was prepared from the ligand **L3** and CoCl₂ according to the literature method [48]. FT-IR (KBr disc, cm⁻¹): 3425, 1618 ($v_{C=N}$), 1578, 1560, 1481, 1435, 1311, 1182, 1161, 1097, 766, 748, 695, 500.

4.3.4. Preparation of CoCl₂(PNHCH₂P) (4)

To a solution of ligand **L4** (0.1500 g, 0.27 mmol) in degassed ethanol (20 mL) was added CoCl₂ (0.035 g, 0.27 mmol), and the reaction mixture was stirred for 3 h at room temperature. Then the solvent was evaporated under reduced pressure and the residue was crushed with diethyl ether. The precipitate was separated, washed diethyl ether and dried in vacuum to give complex **4** as a light green powder (yield: 0.1358 g, 73.8%). FT-IR (KBr disc, cm⁻¹): 3406, 3057, 1623, 1586, 1479, 1437, 1321, 1265, 1117, 1097, 1044, 747, 695, 515. Anal. Calcd for C₃₇H₃₁Cl₂CoNP₂ (681.44): C, 65.21; H, 4.59; N, 2.06. Found: C, 65.61; H, 4.37; N, 1.81.

4.4. Polymerization of butadiene

Solution polymerizations of butadiene in toluene were carried out in a sealed glass reactor (100 mL) with a rubber septum and a connection to a vacuum system. The reactor was charged with the desired amounts of precatalyst and cocatalyst solutions. The mixture was stirred for 2 min at the desired temperature and followed by the addition of a solution of butadiene in toluene. The polymerization reaction was carried out by vigorous stirring of the reaction mixture at the various temperatures. After the polymerization, the resulting solution was poured into a large amount of acidified ethanol (5% v/v solution of HCl) containing 2,6-di-*tert*butyl-4-methylphenol as a stabilizer. The precipitated polymers were filtered, washed with ethanol and dried under vacuum at 50 °C overnight.

4.5. X-ray crystallography measurements

Green crystals of $1a \cdot 3CH_2Cl_2$ suitable for X-ray diffaraction analysis were obtained by slow diffusion of *n*-hexane into its dichloromethane solution. The crystal used for data collection was cut from a needle and gave rather broad diffraction peaks, which has limited the quality of the refinement. Data were collected at 293(2) K on a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All nonhydrogen atoms, except for the solvent molecules, were refined with anisotropic atomic displacement parameters. Hydrogen atoms ere inserted at calculated positions except for the hydrogen (H1A) bound to Cl1, which was located from a difference map and not further refined. Structure solution and refinement were performed by using the SHELXL-97 Package [60]. Crystallographic data and processing parameters for complexes **1a**·3CH₂Cl₂ are summarized in Table 3.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21006085), the State Key Laboratory of Chemical Engineering (Grant No. SKL-ChE-11D03) and National Basic Research Program of China (973 Program, grant No. 2011CB606001).

Appendix A. Supplementary material

CCDC 875645 contains the supplementary crystallographic data for complex **1a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/ data_request/cif.

References

- A. Proto, C. Capacchione, Stereoselective Polymerization with Single-Site Catalysts, CRC Press, Boca Raton, FL, 2008, pp. 447–473.
- [2] G.J. Van Amerongen, Adv. Chem. Ser 52 (1966) 136-152.
- [3] J. Furukawa, Pure Appl. Chem. 42 (1975) 495-508.
- [4] J. Furukawa, Acc. Chem. Res. 13 (1980) 1-6.
- [5] W. Cooper, Ind. Eng. Chem. Prod. Res. Develop 9 (1970) 457–466.
- [6] L. Porri, A. Giarrusso, G. Ricci, Prog. Polym. Sci. 16 (1991) 405-441.
- [7] A. Oehme, U. Gebauer, K. Gehrke, M.D. Lechner, Angew. Makromol. Chem. 235 (1996) 121-130.
- [8] Y. Jang, P. Kim, Y. Jeong, H. Lee, Macromolecules 35 (2002) 1477–1480.
- [9] Y. Jang, P. Kim, Y. Jeong, H. Lee, J. Mol. Catal. A: Chem. 206 (2003) 29–36.
- [10] G. Ricci, A. Forni, A. Boglia, T. Motta, J. Mol. Catal. A: Chem. 226 (2005) 235–241.
- [11] G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti, F. Bertini, Macromolecules 38 (2005) 1064–1070.
- [12] G. Ricci, A. Forni, A. Boglia, A. Sommazzi, F. Masi, J. Organomet. Chem. 690 (2005) 1845–1854.
- [13] G. Ricci, T. Motta, A. Boglia, E. Alberti, L. Zetta, F. Bertini, P. Arosio, A. Famulari, S. Valdo Meille, Macromolecules 38 (2005) 8345–8352.
- [14] G. Ricci, A. Boglia, T. Motta, F. Bertini, A.C. Boccia, L. Zetta, E. Alberti, A. Famulari, P. Arosio, S.V. Meille, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 5339–5353.
- [15] G. Leone, A. Boglia, F. Bertini, M. Canetti, G. Ricci, J. Polym. Sci. Part A: Polym. Chem. 48 (2010) 4473–4483.
- [16] D.C.D. Nath, T. Shiono, T. Ikeda, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 3086–3092.
- [17] D.C.D. Nath, T. Shiono, T. Ikeda, Macromol. Chem. Phys. 204 (2003) 2017-2022.
- [18] K. Endo, N. Hatakeyama, J. Polym. Sci. Part A: Polym. Chem. 39 (2001)
- 2793–2798.
- [19] D.C.D. Nath, T. Shiono, T. Ikeda, Macromol. Chem. Phys. 203 (2002) 756-760.
- [20] D.C.D. Nath, T. Shiono, T. Ikeda, Appl. Catal. A: Gen. 238 (2003) 193-199.
- [21] G. Kwag, C. Bae, S. Kim, J. Appl. Polym. Sci. 113 (2009) 2186–2190.
- [22] Z. Cai, M. Shinzawa, Y. Nakayama, T. Shiono, Macromolecules 42 (2009) 7642-7643.
- [23] R. Taube, G. Sylvester, Applied Homogeneous Catalysis with Organometallic Complexes, Wiley-VCH, Weinheim, Germany, 2002, 285–315.
- [24] S.K.-H. Thiele, D.R. Wilson, J. Macromol. Sci. Part C: Polym. Rev. C43 (2003) 581–628.
- [25] G. Ricci, A. Sommazzi, F. Masi, M. Ricci, A. Boglia, G. Leone, Coord. Chem. Rev. 254 (2010) 661–676 (and references therein).
- [26] W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng, H. Wang, New J. Chem. 26 (2002) 1474–1478.
- [27] X. Tang, D. Zhang, S. Jie, W.-H. Sun, J. Chen, J. Organomet. Chem. 690 (2005) 3918–3928.

- [28] R. Cariou, J. Chirinos, V.C. Gibson, G. Jacobsen, A.K. Tomov, M.R.J. Elsegood, Macromolecules 42 (2009) 1443-1444.
- [29] R. Cariou, J.J. Chirinos, V.C. Gibson, G. Jacobsen, A.K. Tomov, G.J.P. Britovsek, A.J.P. White, Dalton Trans. 39 (2010) 9039-9045.
- S. Jie, P. Ai, B.-G. Li, Dalton Trans. 40 (2011) 10975–10982. [30]
- M.E. Wilson, R.G. Nuzzo, G.M. Whitesides, J. Am. Chem. Soc. 100 (1978) [31] 2269-2270.
- [32] R.G. Nuzzo, S.L. Haynie, M.E. Wilson, G.M. Whitesides, J. Org. Chem. 46 (1981) 2861-2867
- [33] M.I. García-Seijo, A. Habtemariam, S. Parsons, R.O. Gouldb, M.E. García-Fernández, New J. Chem. 26 (2002) 636–644.
- [34] M. Wang, X. Yu, Z. Shi, M. Qian, K. Jin, J. Chen, R. He, J. Organomet. Chem. 645 (2002) 127 - 133.
- [35] D.S. McGuinness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, J.T. Dixon, C. Grove, Chem. Commun. (2003) 334-335.
- D.S. McGuinness, P. Wasserscheid, D.H. Morgan, J.T. Dixon, Organometallics 24 [36] (2005) 552 - 556
- [37] D.S. McGuinness, D.B. Brown, R.P. Tooze, F.M. Hess, J.T. Dixon, A.M.Z. Slawin, Organometallics 25 (2006) 3605-3610.
- D. Walther, T. Döhler, K. Heubach, O. Klobes, B. Schweder, H. Görls, Z. Anorg. [38] Allg. Chem. 625 (1999) 923-932.
- A.N. Marziale, E. Herdtweck, J. Eppinger, S. Schneider, Inorg. Chem. 48 (2009) [39] 3699-3709.
- A. Romerosa, C. Saraiba-Bello, M. Serrano-Ruiz, A. Caneschi, V. McKee, [40] M. Peruzzini, L. Sorace, F. Zanobini, Daton Trans. (2003) 3233-3239.
- [41] B. Rezzonico, M. Grignon-Dubois, J. Chem. Res. (S) (1994) 142-143.
- G. Müller, M. Klinga, M. Leskelä, B. Rieger, Z. Anorg. Allg. Chem. 628 (2002) [42] 2839-2846
- [43] B.L. Small, M. Brookhart, A.M.A. Bennet, J. Am. Chem. Soc. 120 (1998) 4049-4050.

- [44] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849-850.
- [45] E.W. Ainscough, A.M. Brodie, P.D. Buckley, A.K. Burrell, S.M.F. Kennedy, J.M. Waters, J. Chem. Soc. Dalton Trans. (2000) 2663-2671.
- [46] E.W. Ainscough, A.M. Brodie, A.K. Burrell, S.M.F. Kennedy, J. Organomet. Chem. 609 (2000) 2-9.
- [47] E.W. Ainscough, A.M. Brodie, A.K. Burrell, X. Fan, M.J.R. Halstead, S.M.F. Kennedy, J.M. Waters, Polyhedron 19 (2000) 2585–2592
- [48] J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng, X. Lu, Organometallics 25 (2006) 236 - 244.
- [49] G. Ricci, F. Masi, A. Boglia, A. Sommazzi, M. Ricci, Advances in Organometallic Chemistry Research, Nova Publisher, USA, 2007, pp. 1–36.
- D. Chandran, C.H. Kwak, C.S. Ha, I. Kim, Catal. Today 131 (2008) 505–512. [50]
- V. Appukuttan, L. Zhang, C.S. Ha, I. Kim, Polymer 50 (2009) 1150-1158. [51]
- V. Appukuttan, L. Zhang, J.Y. Ha, D. Chandran, B.K. Bahuleyan, C.-S. Ha, I. Kim, [52] J. Mol. Catal. A: Chem. 325 (2010) 84–90.
- P. Ai, L. Chen, Y. Guo, S. Jie, B.-G. Li, J. Organomet. Chem. 705 (2012) 51–58. [53]
- D. Gong, X. Jia, B. Wang, X. Zhang, L. Jiang, J. Organomet. Chem. 702 (2012) 10–18.
 C. Bianchini, G. Giambastiani, I.G. Rios, G. Mantovani, A. Meli, A.M. Segarra, Coord. Chem. Rev. 250 (2006) 1391–1418 (and references therein). [54]
- [56] V.C. Gibson, C. Redshaw, G.A. Solan, Chem. Rev. 107 (2007) 1745-1776 (and references therein)
- [57] C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, Coord. Chem. Rev. 254 (2010) 431-455 (and references therein).
- J.E. Hoots, T.B. Rauchfuss, D.A. Wrobleski, Inorg. Synth. 21 (1982) 175-178. [58]
- [59] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, J. Organomet. Chem. 522 (1996) 69 - 76
- [60] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.