Article

Highly active and *cis*-1,4 selective polymerization of 1,3-butadiene catalyzed by cobalt(II) complexes bearing α-diimine ligands

Xiangyu Jia [a,b], Heng Liu [a,b], Yanming Hu [c,#], Quanquan Dai [a], Jifu Bi [a], Chenxi Bai [a], Xuequan Zhang [a,*]

[a] *Research Center of High Performance Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, Liaoning, China*

ABSTRACT

A series of cobalt(II) complexes bearing α-diimine ligands were synthesized and characterized by elemental and spectroscopic analysis. These complexes had the general formulas [ArN=C(Me)–(Me)C=NAr]CoCl$_2$ (Ar = C$_6$H$_5$, **3a**; 4-MeC$_6$H$_4$, **3b**; 4-MeOC$_6$H$_4$, **3c**; 4-FC$_6$H$_4$, **3d**; 4-ClC$_6$H$_4$, **3e**; 2-MeC$_6$H$_4$, **3f**; 2-EtC$_6$H$_4$, **3g**; 2-^{i}PrC$_6$H$_4$, **3h**; 2,4,6-Me$_3$C$_6$H$_2$, **3i**; 2,6-Et$_2$C$_6$H$_3$, **3j**; 2,6-^{i}PrC$_6$H$_3$, **3k**). 2,6-Bis[(2,6-diisopropylphenylimino)ethyl]pyridine CoCl$_2$ (**4a**) was also synthesized for comparison. The structures of complexes **3i**, **3k**, and **4a** were further analyzed by X-ray crystallography. When the Co(II) complexes were activated with ethylaluminum sesquichloride, they exhibited high catalytic activity for 1,3-butadiene polymerization. The polymers produced have high *cis*-1,4 stereoregularity (up to 98.0%) and high molecular weights ($M_n = 1 \times 10^4 – 1 \times 10^5$). The substituent ligand affected both catalytic activity and stereoselectivity through an electronic effect while steric hindrance by the substituent was not important. The effects of the polymerization conditions, such as polymerization time, temperature, different alkylaluminum compounds used as cocatalyst, and [Al]/[Co] molar ratio, on polymerization behavior were investigated.

1. Introduction

The stereoselective polymerization of conjugated dienes, especially 1,3-butadiene and isoprene, by transition metal catalysts for producing high performance synthetic rubber is of substantial interest [1–7]. Polybutadiene is an important polymer with extensive and diverse applications that depend on its microstructure [8]. Numerous catalysts based on transition metals (Ti, Ni, Co, etc.) and rare earth metals have been developed to selectively produce *cis*-1,4- [9–21], *trans*-1,4- [22–25], and 1,2-polybutadienes [26–32]. The addition of Lewis bases

plays an important role in controlling stereoselectivity [33,34]. *Cis*-1,4 selective polymerization of 1,3-butadiene is important because the product, *cis*-1,4-polybutadiene, is a major raw material in the tire industry. Industrially, high *cis*-1,4-polybutadiene is obtained by utilizing conventional Ziegler-Natta catalysts based on transition metals or rare earth metals, such as Ni(naph)$_2$/BF$_3$·Et$_2$O/AlEt$_3$ [35], CoCl$_2$/AlEt$_2$Cl [36], TiCl$_4$/I$_2$/Al(i-Bu)$_3$ [37], or Nd(vers)$_3$/Al(i-Bu)$_2$H/Al$_2$Et$_3$Cl$_3$ [38].

Among the above catalyst systems, Co-based catalysts have attracted special attention because they can produce polybutadienes with tunable structures, such as *cis*-1,4- and syndiotactic

1,2-isomers, which are determined by the structure of the ligand on the Co metal center. Various Co catalysts have been designed to polymerize 1,3-butadiene selectively. For example, cobalt halides and carboxylates activated with methylaluminoxane (MAO) can give high *cis*-1,4-polybutadiene, and CoCl2/MAO catalysts with alkylphosphine adducts are effective for 1,2-selective polymerization of 1,3-butadiene [39–41]. Although these catalysts can produce polybutadienes with high stereoregularity, their active sites are not uniform, and the molecular weight distribution of the polybutadienes is broad. Also, it has not been clarified how the structure of the catalyst precursors affect the polymerization behavior. Recent studies have focused on well defined homogeneous single site organometallic catalysts. These studies are primarily an empirical search for understanding the catalyst structure that determines catalytic activity and stereoselectivity. For example, four-coordinated (salen)Co(II) ([ONNO]$^{2-}$) [42] and bis(salicylaldiminate)Co(II) ([NO]$^-_2$) [43] complexes activated with MAO or ethylaluminum sesquichloride (EASC) exhibited both high catalytic activity and *cis*-1,4 selectivity for 1,3-butadiene polymerization. Some three-coordinated catalysts, such as bis(imino)pyridine Co(II) [44], bis(benzimidazolyl)amine Co(II) [34], bis(benzimidazolyl) pyridine Co(II) [45,46], bis(thiazolinyl)pyridine Co(II) [47], 2-arylimino-6-(alcohol)pyridine/2-arylamino-6-(alcohol) pyridine Co(II) [48], and 3-aryliminomethyl-2-hydroxybenzaldehyde Co(II) [49] complexes, activated with alkylaluminum cocatalysts also displayed high catalytic activity and high *cis*-1,4 selectivity. In our previous study [44], we found that the incorporation of electron-withdrawing groups into the imino ligands enhanced both the catalytic activity and selectivity of a bis(imino)pyridine Co(II)/MAO catalyst for 1,3-butadiene polymerization. Steric hindrance by the substituent on the ligand also influenced the polymerization behavior to some extent.

In 1995, a new type of catalyst based on Ni and Pd complexes bearing *α*-diimine ligands was discovered by Brookhart and coworkers [50] for producing high molecular weight polyethylene and linear *α*-olefins. These bidentate ligands are very rigid, and it is possible to easily change their backbone and change the electronic effect at the metal center. In ethylene polymerization, when the steric hindrance of the aryl groups attached to the imino nitrogens is reduced, the product composition is shifted from high molecular weight polymer towards linear oligomers [51,52]. However, [NN] bidentate Co(II) complexes for 1,3-butadiene polymerization have not been reported yet. Compared with the [NNN] tridentate ligand, the *α*-diimine ligand gives the metal complex a more open coordinated environment due to less steric hindrance. Thus, it is expected that these Co complexes would display interesting 1,3-butadiene polymerization behavior, which may be different from that of the [NNN] tridentate complexes.

In this study, in order to understand how the ligand affects catalytic behavior, we report the synthesis and characterization of (*α*-diimine)Co(II) complexes and used 2,6-bis[(2,6- diisopropylphenylimino)ethyl]pyridine Co(II) dichloride for comparison. The influences of the ligand structure, polymerization time, alkylaluminum compound, [Al]/[Co] molar ratio, and polymerization temperature on the polymerization of 1,3-butadiene were investigated in detail.

2. Experimental

2.1. General considerations and materials

All manipulations were carried out under N2 atmosphere using standard Schlenk techniques. Fourier-transform infrared spectroscopy (FT-IR) was performed on a Bruker Vertex-70 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-400 spectrometer with CDCl3 at room temperature and tetramethylsilane as the internal standard. Elemental analyses were recorded on an elemental Vario EL spectrometer. The proportions of *cis*-1,4-, *trans*-1,4- and 1,2-units of the polymer were determined from the IR, ^{1}H NMR, and ^{13}C NMR spectra [53,54]. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer 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 × 2, HMW 2 THF), and a Waters 2414 refractive index detector. Tetrahydrofuran (1.0 ml/min) was used as the eluent.

Toluene was refluxed over sodium-benzophenone and distilled under N2 prior to use. MAO (1.5 mol/L in toluene) was purchased from Akzo Nobel Corp. Diethylaluminium chloride (DEAC, 0.9 mol/L in toluene) was purchased from Alfa Aesar and used without further purification. EASC was purchased from Sigma-Aldrich Co. and diluted into toluene solution (1.16 mol/L) before use. Polymerization grade 1,3-butadiene was purified by passing it through KOH and molecular sieve columns. CoCl2, 2,3-butanedione, 2,6-diacetylpyridine, and various anilines were purchased from Alfa Aesar and used without further purification.

2.2. Synthesis and characterization of the ligands and Co(II) complexes

Ligands **2a**–**2k**, 2,6-bis[(2,6-diisopropylphenylimino)ethyl] pyridine, and the corresponding complexes **3a**–**3k** and **4a** were synthesized according to the literature [11,36,48–50,55–57].

For synthesis of ligand **2a**, a reaction mixture of 2,3-butanedione (2.0 g, 0.023 mol), aniline (4.33 g, 0.047 mol), a few drops of formic acid and methanol (20 ml) was refluxed for 12 h and cooled to room temperature. A yellow crystal-like solid precipitated after several hours. The desired product (4.2 g, 76.5%) was identified by FT-IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis. ^{1}H NMR (400 MHz, CDCl3, *δ*): 7.368 (t, 4H, *J* = 7.6 Hz, H_{aryl}), 7.112 (t, 2H, *J* = 7.6 Hz, H_{aryl}), 6.798 (d, 4H, *J* = 7.6 Hz, H_{aryl}), 2.150 (s, 6H, –C(CH_3)=N–). ^{13}C NMR (100 MHz, CDCl3, *δ*): 168.22 (N=*C*), 150.93 (*C*$_{Ar}$–N), 128.95, 123.78, 118.71, 15.34 (N=C*C*H3). IR (KBr, cm^{-1}): 1635 ($\nu_{C=N}$), 1480, 1445, 1355, 1207, 1116, 1071, 809, 762, 695. Anal. Calcd for C16H16N2: C 81.32, H 6.82, N 11.86; Found: C 81.53, H 6.75, N 11.81.

For synthesis of ligand **2b**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 4-methylaniline (5.0 g, 0.047 mol), yield 5.06 g (83.2%). ^{1}H NMR (400 MHz,

CDCl$_3$, δ): 7.175 (d, 4H, J = 7.6 Hz, H_{aryl}), 6.70 (d, 4H, J = 8.0 Hz, H_{aryl}), 2.347 (s, 6H, –CH_3), 2.148 (s, 6H, –C(CH_3)=N–). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.29 (N=C), 148.35 (C_{Ar}–N), 133.21, 129.45, 118.84, 20.82 (Ar–CH$_3$), 15.29 (N=CCH$_3$). IR (KBr, cm^{-1}): 1628 ($\nu_{C=N}$), 1501, 1431, 1362, 1204, 1116, 1040, 810, 746, 709. Anal. Calcd for C$_{18}$H$_{20}$N$_2$: C 81.78, H 7.63, N 10.60; Found: C 81.54, H 7.88, N 10.56.

For synthesis of ligand **2c**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.0232 mol), 4-methoxyaniline (5.72 g, 0.0464 mol), yield 5.15 g (75.6%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.930 (d, 4H, J = 8.4 Hz, H_{aryl}), 6.775 (d, 4H, J = 8.4 Hz, H_{aryl}), 3.818 (s, 6H, –OCH_3), 2.176 (s, 6H, –C(CH_3)=N–). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.39 (N=C), 156.37 (C_{Ar}–N), 144.01, 120.50, 114.17, 55.40 (Ar–OCH$_3$), 15.32 (N=CCH$_3$). IR (KBr, cm^{-1}): 1633 ($\nu_{C=N}$), 1501, 1440, 1356, 1205, 1116, 1035, 842, 756, 710. Anal. Calcd for C$_{18}$H$_{20}$N$_2$O$_2$: C 72.95, H 6.80, N 9.45; Found: C 73.06, H 6.71, N 9.47.

For synthesis of ligand **2d**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.0232 mol), 4-fluoroaniline (5.16 g, 0.0464 mol), yield 6.02 g (96.2%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.068 (t, 4H, J = 8.8 Hz, H_{aryl}), 6.736–6.770 (m, 4H, H_{aryl}), 2.146 (s, 6H, –C(CH_3)=N–). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.81 (N=C), 160.87 (d, J_{CF} = 242 Hz), 146.72 (C_{Ar}–N), 120.31, 115.78, 15.29 (N=CCH$_3$). IR (KBr, cm^{-1}): 1649 ($\nu_{C=N}$), 1497, 1431, 1356, 1198, 1123, 1093, 852, 758, 708. Anal. Calcd for C$_{16}$H$_{14}$F$_2$N$_2$: C 70.58, H 5.18, N 10.29; Found: C 70.46, H 5.23, N 10.33.

For synthesis of ligand **2e**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 4-chloroaniline (5.93 g, 0.046 mol), yield 4.56 g (64.9%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.346 (d, 4H, J = 8.4 Hz, H_{aryl}), 6.734 (d, 4H, J = 8.4 Hz, H_{aryl}), 2.129 (s, 6H, –C(CH_3)=N–). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.66 (N=C), 149.20, 132.46, 129.05, 120.17, 15.35 (N=CCH$_3$). IR (KBr, cm^{-1}): 1634 ($\nu_{C=N}$), 1480, 1431, 1360, 1205, 1121, 1086, 845. Anal. Calcd for C$_{16}$H$_{14}$Cl$_2$N$_2$: C 62.97, H 4.62, N 9.18; Found: C 63.06, H 4.71, N 9.32.

For synthesis of ligand **2f**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2-methylaniline (5.0 g, 0.047 mol), yield 5.08 g (83.6%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.175–7.251 (quintet, 4H, H_{aryl}), 7.033 (t, 2H, J = 7.6 Hz, H_{aryl}), 6.657 (d, 2H, J = 8.0 Hz, H_{aryl}), 2.119 (s, 12H, –C(CH_3)=N–, –CH_3). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 167.65 (N=C), 149.46 (C_{Ar}–N), 130.36, 126.32, 123.43, 117.58, 17.69 (Ar–CH$_3$), 15.49 (N=CCH$_3$). IR (KBr, cm^{-1}): 1640 ($\nu_{C=N}$), 1484, 1452, 1355, 1216, 1118, 1042, 855, 782, 717. Anal. Calcd for C$_{18}$H$_{20}$N$_2$: C 81.78, H 7.63, N 10.60; Found: C 81.53, H 7.71, N 10.77.

For synthesis of ligand **2g**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2-ethylaniline (5.63 g, 0.047 mol), yield 6.23 g (92.7%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.272–7.290 (d, 2H, J = 8 7.2 Hz, H_{aryl}), 7.197 (t, 2H, J = 7.6 Hz, H_{aryl}), 7.077 (t, 2H, J = 7.6 Hz, H_{aryl}), 6.639 (d, 2H, J = 7.6 Hz, H_{aryl}), 2.464–2.520 (q, 4H, –CH_2CH$_3$), 2.141 (s, 6H, –C(CH_3)=N–), 1.160 (t, 6H, J = 7.2 Hz, –CH$_2$CH_3). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 167.59 (N=C), 148.90 (C_{Ar}–N), 133.06, 128.62, 126.27, 124.09, 117.71, 24.70 (–CH$_2$CH$_3$), 15.52 (N=CCH$_3$), 13.97 (–CH$_2$$CH_3$). IR (KBr, cm^{-1}): 1640 ($\nu_{C=N}$), 1481, 1460, 1361,

1242, 1116, 1050, 821, 752. Anal. Calcd for C$_{20}$H$_{24}$N$_2$: C 82.15, H 8.27, N 9.58; Found: C 82.47, H 8.41, N, 9.53.

For synthesis of ligand **2h**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2-isopropylaniline (6.28 g, 0.046 mol), yield 6.67 g (90.5%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.327 (d, 2H, J = 7.2 Hz, H_{aryl}), 7.182 (t, 2H, J = 7.2 Hz, H_{aryl}), 7.112 (t, 2H, J = 7.2 Hz, H_{aryl}), 6.616 (d, 2H, J = 7.6 Hz, H_{aryl}), 2.912–3.015 (sept, 2H, –CH(CH$_3$)$_2$, 2.159 (s, 6H, –C(CH_3)=N–), 1.209 (d, 12H, J = 6.8 Hz, –CH(CH_3)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 167.55 (N=C), 148.26 (C_{Ar}–N), 137.75, 126.05, 125.64, 124.27, 117.86, 28.48 (–CH(CH$_3$)$_2$), 22.68 (–CH(CH$_3$)$_2$), 15.63 (N=CCH$_3$). IR (KBr, cm^{-1}): 1633 ($\nu_{C=N}$), 1482, 1446, 1357, 1281, 1115, 1032, 813, 752. Anal. Calcd for C$_{22}$H$_{28}$N$_2$: C 82.45, H 8.81, N 8.74; Found: C 82.54, H 8.92, N 8.67.

For synthesis of ligand **2i**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2,4,6-trimethylaniline (6.28 g, 0.046 mol), yield 7.13 g (96.8%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.886 (s, 4H, H_{aryl}), 2.284 (s, 6H, –C(CH_3)=N–), 2.024 (s, 6H, –CH_3), 1.995 (s, 12H, –CH_3). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.30 (N=C), 145.86 (C_{Ar}–N), 132.35, 128.54, 124.49, 20.68, 17.67, 15.73 (N=CCH$_3$). IR (KBr, cm^{-1}): 1637 ($\nu_{C=N}$), 1478, 1433, 1360, 1211, 1120, 1035, 856, 790, 726. Anal. Calcd for C$_{22}$H$_{28}$N$_2$: C 82.45, H 8.81, N 8.74; Found: C 82.56, H 8.53, N 8.78.

For synthesis of ligand **2j**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2,6-diethylaniline (6.93 g, 0.046 mol), yield 7.66 g (95.5%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.116 (d, 4H, J = 7.6 Hz, H_{aryl}), 7.024 (t, 2H, J = 6.8 Hz, H_{aryl}), 2.30–2.447 (nonuple, 8H, –CH_2CH$_3$), 2.053 (s, 6H, –C(CH_3)=N–), 1.158 (t, 12H, J = 7.6 Hz, –CH$_2$CH_3). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 167.93 (N=C), 147.39 (C_{Ar}–N), 130.48, 126.06, 123.48, 24.68, 16.13 (N=CCH$_3$), 13.60. IR (KBr, cm^{-1}): 1643 ($\nu_{C=N}$), 1448, 1362, 1188, 1036, 872, 800, 763. Anal. Calcd for C$_{24}$H$_{32}$N$_2$: C 82.71, H 9.25, N 8.04; Found: C 82.67, H 9.17, N 8.06.

For synthesis of ligand **2k**, a procedure similar to **2a** was adopted. 2,3-Butanedione (2.0 g, 0.023 mol), 2,6-diisopropylaniline (8.24 g, 0.046 mol), yield 6.82 g (73.3%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.177 (d, 4H, J = 7.2 Hz, H_{aryl}), 7.096 (t, 2H, J = 6.8 Hz, H_{aryl}), 2.663–2.766 (sept, 4H, –CH(CH$_3$)$_2$), 2.068 (s, 6H, –C(CH_3)=N–), 1.186 (t, 24H, J = 8.0 Hz, –CH(CH_3)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.15 (N=C), 146.16 (C_{Ar}–N), 135.02, 123.72, 122.97, 28.48, 22.67, 16.54 (N=CCH$_3$). IR (KBr, cm^{-1}): 1639 ($\nu_{C=N}$), 1438, 1363, 1181, 1160, 1041, 792, 763. Anal. Calcd for C$_{28}$H$_{40}$N$_2$: C 83.11, H 9.96, N 6.92; Found: C 83.06, H 10.13, N 6.98.

For synthesis of 2,6-bis[[(2,6-diisopropylphenylimino)ethyl] pyridine, a procedure similar to **2a** was adopted. 2,6-Diacetylpyridine (1.5 g, 0.009 mol), 2,6-diisopropylaniline (3.46 ml, 0.018 mol), yield 3.26 g (75.2%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.502 (d, 2H, J = 8Hz, H_{Py}), 7.934 (t, 1H, J = 8Hz, H_{Py}), 7.091–7.168 (m, 6H, H_{aryl}), 2.783 (sept, 4H, J = 5.6 Hz, –CH(CH$_3$)$_2$), 2.268 (s, 6H, –C(CH_3)=N–), 1.182 (d, 24H, –CH(CH_3)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 166.85, 155.10, 146.46, 136.80, 135.72, 123.52, 122.95, 122.14, 28.25, 22.84, 17.07. IR (KBr, cm^{-1}): 1644 ($\nu_{C=N}$), 1454, 1254, 1122, 766. Anal.

Calcd for $C_{33}H_{43}N_3$: C 82.28, H 9.00, N 8.72; Found: C 82.16, H 9.23, N 8.63.

For synthesis of complex **3a**, a mixture of **2a** (0.25 g, 0.001 mol) and anhydrous $CoCl_2$ (0.137 g, 0.001 mol) were added to a flask containing THF (10 ml). The mixture was stirred at room temperature for 12 h, during which a green suspension was formed. Diethyl ether was added and the precipitate was collected by filtration and washed with 4 × 5 ml heptane. The product (0.21g, 54.3%) was obtained after drying in vacuo at 40 °C. IR (KBr, cm⁻¹): 1644 ($\nu_{C=N}$), 1486, 1449, 1363, 1244, 1143, 1074, 846, 814, 765. Anal. Calcd for $C_{16}H_{16}Cl_2CoN_2$: C 52.48, H 4.40, N 7.65; Found: C 52.62, H 4.77, N 7.56.

For synthesis of complex **3b**, a procedure similar to **3a** was adopted using **2b** and $CoCl_2$, which gave **3b** as a green powder in 72.6% yield (0.31 g). IR (KBr, cm⁻¹): 1644 ($\nu_{C=N}$), 1509, 1421, 1373, 1246, 1144, 1037, 839, 781, 713. Anal. Calcd for $C_{18}H_{20}Cl_2CoN_2$: C 54.84, H 5.11, N 7.11; Found: C 54.95, H 5.17, N 6.94.

For synthesis of complex **3c**, a procedure similar to **3a** was adopted using **2c** and $CoCl_2$, which gave **3c** as a green powder in 56.1% yield (0.24 g). IR (KBr, cm⁻¹): 1638 ($\nu_{C=N}$), 1507, 1442, 1374, 1171, 1143, 1037, 875, 785, 719. Anal. Calcd for $C_{18}H_{20}Cl_2CoN_2O_2$: C 50.73, H 4.73, N 6.57; Found: C 51.06, H 4.82, N 6.51.

For synthesis of complex **3d**, a procedure similar to **3a** was adopted using **2d** and $CoCl_2$, which gave **3d** as a green powder in 82.4% yield (0.33 g). IR (KBr, cm⁻¹): 1644 ($\nu_{C=N}$), 1500, 1423, 1375, 1215, 1142, 1091, 869, 785, 712. Anal. Calcd for $C_{16}H_{14}Cl_2CoF_2N_2$: C 47.79, H 3.51, N 6.97; Found: C 48.01, H 3.82, N 6.82.

For synthesis of complex **3e**, a procedure similar to **3a** was adopted using **2e** and $CoCl_2$, which gave **3e** as a green powder in 93.7% yield (0.41 g). IR (KBr, cm⁻¹): 1648 ($\nu_{C=N}$), 1483, 1421, 1377, 1237, 1143, 1008, 864. Anal. Calcd for $C_{16}H_{14}Cl_4CoN_2$: C 44.17, H 3.24, N 6.44; Found: C 44.29, H 3.38, N 6.35.

For synthesis of complex **3f**, a procedure similar to **3a** was adopted using **2f** and $CoCl_2$, which gave **3f** as a green powder in 76.2% yield (0.30 g). IR (KBr, cm⁻¹): 1637 ($\nu_{C=N}$), 1487, 1460, 1373, 1233, 1113, 1047, 866, 813, 712. Anal. Calcd for $C_{18}H_{20}Cl_2CoN_2$: C 54.84, H 5.11, N 7.11; Found: C 55.17, H 5.27, N 7.04.

For synthesis of complex **3g**, a procedure similar to **3a** was adopted using **2g** and $CoCl_2$, which gave **3g** as a green powder in 86.4% yield (0.36 g). IR (KBr, cm⁻¹): 1639 ($\nu_{C=N}$), 1482, 1459, 1362, 1243, 1117, 1051, 821, 751. Anal. Calcd for $C_{20}H_{24}Cl_2CoN_2$: C 56.89, H 5.73, N 6.63; Found: C 57.12, H 5.88, N 6.47.

For synthesis of complex **3h**, a procedure similar to **3a** was adopted using **2h** and $CoCl_2$, which gave **3h** as a green powder in 92.6% yield (0.42 g). IR (KBr, cm⁻¹): 1635 ($\nu_{C=N}$), 1481, 1444, 1359, 1280, 1116, 1031, 812, 751. Anal. Calcd for $C_{22}H_{28}Cl_2CoN_2$: C 58.68, H 6.27, N 6.22; Found: C 58.96, H 6.60, N 6.00.

For synthesis of complex **3i**, a procedure similar to **3a** was adopted using **2i** and $CoCl_2$, which gave **3i** as a green powder in 88.9% yield (0.40 g). IR (KBr, cm⁻¹): 1635 ($\nu_{C=N}$), 1477, 1437, 1359, 1210, 1122, 1038, 857, 791, 727. Anal. Calcd for $C_{26}H_{36}Cl_2CoN_2O$: C 59.78, H 6.95, N 5.36; Found: C 59.95, H 7.14, N 5.17.

For synthesis of complex **3j**, a procedure similar to **3a** was adopted using **2j** and $CoCl_2$, which gave **3j** as a green powder in 72.5% yield (0.35 g). IR (KBr, cm⁻¹): 1641 ($\nu_{C=N}$), 1449, 1361, 1189, 1038, 870, 803, 765. Anal. Calcd for $C_{24}H_{32}Cl_2CoN_2$: C 60.26, H 6.74, N 5.86; Found: C 60.55, H 6.92, N 5.61.

For synthesis of complex **3k**, a procedure similar to **3a** was adopted using **2k** and $CoCl_2$, which gave **3k** as a green powder in 81.6% yield (0.44 g). IR (KBr, cm⁻¹): 1638 ($\nu_{C=N}$), 1443, 1364, 1211, 1184, 1043, 788, 762. Anal. Calcd for $C_{28}H_{40}Cl_2CoN_2$: C 62.92, H 7.54, N 5.24; Found: C 63.18, H 7.76, N 5.03.

For synthesis of complex **4a**, a procedure similar to **3a** was adopted using 2,6-bis[(2,6-diisopropylphenylimino)ethyl]pyridine and $CoCl_2$, which gave **4a** as a brown powder in 93.7% yield (0.57 g). IR (KBr, cm⁻¹): 1617, 1467, 1264, 1104, 780. Anal. Calcd for $C_{33}H_{43}Cl_2CoN_3$: C 64.81, H 7.09, N 6.87; Found: C 65.17, H 7.44, N 6.63.

2.3. 1,3-Butadiene polymerization

A typical procedure for the polymerization is as follows. A toluene solution of 1,3-butadiene (1 g, 1.85 × 10⁻² mol) was added to a moisture-free ampoule bottle preloaded with complex **3a** (3.4 mg, 9.25 × 10⁻⁶ mol). Then, EASC (1.16 × 10⁻³ mol/ml, 0.2 ml) was injected to initiate the polymerization at 20 °C. After 30 min, methanol was added to the system to quench the polymerization. The mixture was poured into a large quantity of methanol containing 2,6-di-tertbutyl-4-methylphenol (1.0%) as a stabilizer. After filtering and drying under vacuum at 40 °C, polybutadiene was obtained (0.918 g, 91.8%).

2.4. X-ray crystallography

Single crystals of **3i**, **3k**, and **4a** suitable for X-ray diffraction (XRD) were obtained by the slow diffusion of diethyl ether into the THF solution. Data collection was performed at –88 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite monochromated Mo K_α radiation (λ = 0.071073 nm). The determination of the crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full matrix least squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The crystallographic and refinement data are summarized in Table 1.

3.　Results and discussion

3.1. Synthesis and characterization of the ligands and Co(II) complexes

The *α*-diimine ligands **2a**–**2k** were synthesized in high yields by the condensation reaction of 2,3-butadione with the corresponding aniline derivatives in the presence of a catalytic

Table 1
Crystal data and data collection parameters for the cobalt complexes.

Complex	3i·THF	3k	4a·H₂O
Formula	$C_{26}H_{36}Cl_2CoN_2O$	$C_{28}H_{40}Cl_2CoN_2$	$C_{33}H_{45}Cl_2CoN_3O$
Molecular weight	522.40	534.45	629.55
Wavelength (nm)	0.071073	0.071073	0.071073
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$	$Pnma$	$P1$
a (nm)	1.30523 (9)	1.25882 (9)	0.86539 (8)
b (nm)	1.43998 (10)	2.13733 (16)	0.98630 (9)
c (nm)	1.44271 (10)	1.04173 (8)	2.08347 (18)
α (°)	90.00	90	84.147 (1)
β (°)	91.059 (1)	90	88.312 (1)
γ (°)	90.00	90	65.634 (1)
V (nm³)	2.7111 (3)	2.8028 (4)	1.6113 (3)
Z	4	4	2
D_{calcd} (mg/m³)	1.280	1.267	1.298
Absorption coefficient (mm⁻¹)	0.85	0.82	0.728
F (000)	1100	1132	666
Crystal size (mm)	0.31 × 0.25 × 0.14	0.28 × 0.19 × 0.10	0.31 × 0.18 × 0.11
θ range (°)	2.8–25.4	2.2–21.9	2.6–26.0
No. of reflcns collected	16613	15802	8579
No. of independent reflcns	5325	2559	6201
No. of data/restraints /params	5325/0/297 (R_{int} = 0.034)	2559/0/159 (R_{int} = 0.054)	6201/0/371 (R_{int} = 0.015)
Goodness-of-fit on F^2	1.050	1.054	1.099
R_1 (1> 2sigma(1))	0.043	0.038	0.045
wR_2	0.108	0.091	0.125

amount of formic acid (Scheme 1). All the ligands were identified by FT-IR, elemental analysis, and ¹H NMR and ¹³C NMR. The α-diimine Co(II) complexes **3a–3k** were prepared by the reaction of the ligands with anhydrous CoCl₂ in THF. All the complexes were isolated as green air-stable powder in high yield and high purity by precipitation from THF and washing with heptane. In the FT-IR spectra, the C=N groups of the free ligands **2a–2k** displayed stretching frequencies at 1628–1649 cm⁻¹, while the absorption peaks of the C=N groups in complexes **3a–3k** were shifted to lower or higher frequencies, and the intensities of the corresponding peaks were greatly reduced. This indicated the occurrence of the coordination reaction between the α-diimine nitrogen atoms and the metal ions. 2,6-Bis[(2,6-diisopropylphenylimino)ethyl]pyridine and its Co complex **4a** were synthesized according to the literature [44]. The structures of complexes **3i**, **3k**, and **4a** were further studied by XRD analysis.
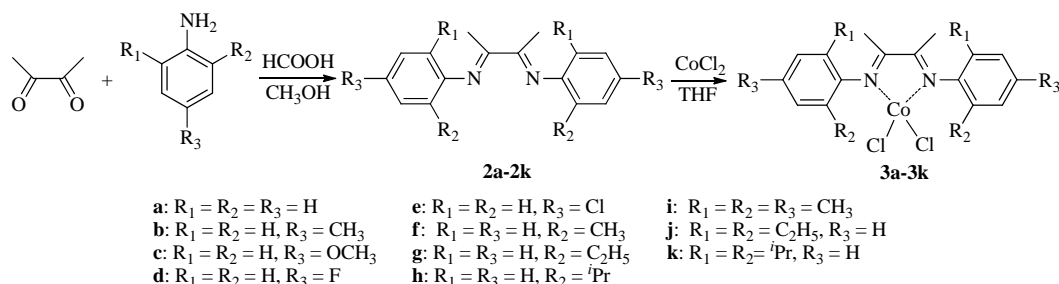
3.2. X-ray structures of *3i*, *3k*, and *4a*

The molecular structures of **3i**, **3k**, and **4a** are shown in Figs. 1–3. Complex **3i** crystallized in the monoclinic space group $P2_1/c$. The Co atom is in a deformed tetrahedron comprising two Cl atoms and two N atoms of the ligand. The dihedral angle formed by the planes defined by Cl1–Co1–Cl2 and N1–Co1–N2 is 86.73°. The Cl1–Co1–Cl2 angle is 114.55(3)°, and the N1–Co1–N2 angle is 79.55(8)°. The Co–Cl bond distances are 0.22140(8) nm and 0.22199(8) nm, and the Co–N bonds are 0.20444(19) nm and 0.20455(19) nm. The [Co1–N1–C1–C2–N2] plane is nearly planar (maximum deviation from least squares plane is 0.0044 nm). The angle between the two phenyl groups is 19.48°, and these groups are perpendicular to the central plane [Co–N1–C1–C2–N2] with angles of 89.07° and 88.05°, respectively.

Complex **3k** displayed a deformed tetrahedral geometry around the Co center with the equatorial plane defined by Co and two Cl atoms. It crystallizes in the orthorhombic space group $Pnma$. The deformed tetrahedral site around the Co atom is characterized by the following distances and angles: Co1–Cl1, 0.22037(10) nm; Co1–Cl2, 0.22159(10) nm; Co1–N1, 0.20560(18) nm; Co1–NlA, 0.20560(18) nm; Cl1–Co1–Cl2, 111.67(4)°; N1–Co1–N1A, 79.34(10)°. Compared with **3i**, the plane containing the Co atom is not well fitted by the least-squares planes calculated, with a maximum deviation from the plane of 0.0094 nm. The angle between the two phenyl groups is 15.07°, and these groups are nearly perpendicular to the central plane [Co1–N1–C2–C2A–N1A] with angles of 84.1°.

Complex **4a** crystallized in the triclinic space group $P1$. The deviation of the Co atom from the N₃ plane 0.0507 nm has an approximate C_s molecular symmetry about a plane bisecting the central pyridine ring and containing the metal atom and two halogen atoms. The Co–N(pyridyl) bond distance in **4a** is 0.2051(2) nm, which is almost the same as the Co–N bonds in **3i** and **3k**. Both of the two Co–N(imino) bond distances are 0.2206(2) nm, obviously larger than those of **3i** and **3k**. The angle of Cl1–Co–Cl2 is 116.53(3)°. The distances of Co–Cl bonds (0.22589(8) and 0.22951(8) nm) are longer than those of **3i** (0.22140(8) and 0.22199(8) nm) and **3k** (0.2159 and 0.22031 nm).

3.3. Solution polymerization of 1,3-butadiene

Co-based complexes with a variety of *ortho-* or *para*-substituted α-diimine ligands were employed to examine the

Scheme 1. Synthesis of ligands **2a–2k** and Co complexes **3a–3k**.

a: R₁ = R₂ = R₃ = H
b: R₁ = R₂ = H, R₃ = CH₃
c: R₁ = R₂ = H, R₃ = OCH₃
d: R₁ = R₂ = H, R₃ = F
e: R₁ = R₂ = H, R₃ = Cl
f: R₁ = R₃ = H, R₂ = CH₃
g: R₁ = R₃ = H, R₂ = C₂H₅
h: R₁ = R₃ = H, R₂ = ⁱPr
i: R₁ = R₂ = R₃ = CH₃
j: R₁ = R₂ = C₂H₅, R₃ = H
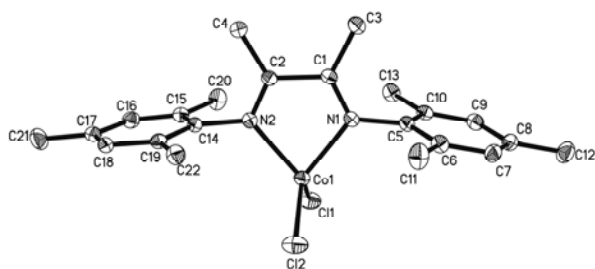**k**: R₁ = R₂ = ⁱPr, R₃ = H

Fig. 1. ORTEP view of complex **3i** drawn at 35% probability. The hydrogen atoms and one THF molecule are omitted for clarity. Selected bond distances (nm): Co1–N1 0.20444(19), Co1–N2 0.20455(19), Co1–Cl1 0.22140(8), Co1–Cl2 0.22199(8). Selected bond angles (°): N1–Co–N2 79.55(8), Cl1–Co–Cl2 114.55(3), N1–Co1–Cl1 113.06(6), N2–Co1–Cl1 116.73(6), N1–Co1–Cl2 116.27(6), N2–Co1–Cl2 112.20(6).
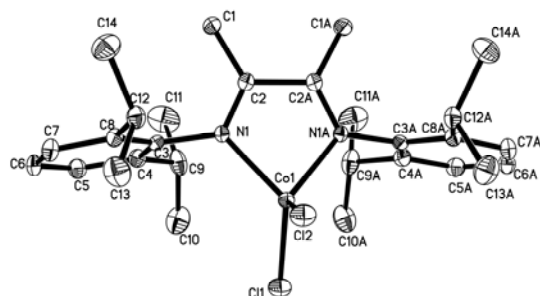

Fig. 2. ORTEP view of complex **3k** drawn at 35% probability. The hydrogen atoms are omitted for clarity. Selected bond distances (nm): Co1–N1 0.20560(18), Co1–N2 0.20560(18), Co1–Cl1 0.22037(10), Co1–Cl2 0.22159(10). Selected bond angles (°): N1–Co–N2 79.34(10), Cl1–Co–Cl2 111.67(4), N1–Co1–Cl1 113.68(5), N2–Co1–Cl1 117.51(5), N1–Co1–Cl2 117.51(5), N2–Co1–Cl2 113.68(5).
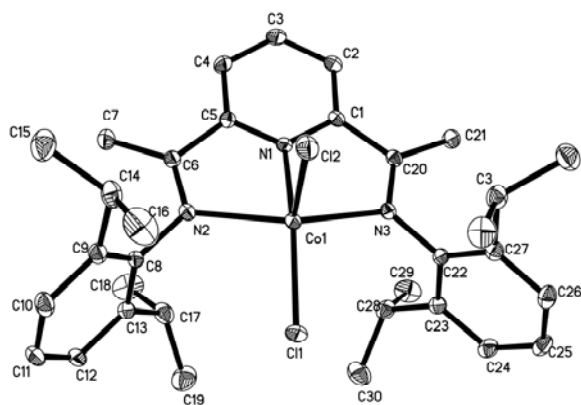

Fig. 3. ORTEP view of complex **4a** drawn at 35% probability. The hydrogen atoms and one H_2O molecule are omitted for clarity. Selected bond distances (nm): Co1–N1 0.2051(2), Co1–N2 0.2206(2), Co1–N3 0.2206(2), Co1–Cl1 0.22589(8), Co1–Cl2 0.22951(8). Selected bond angles (°): N1–Co–N2 74.04(8), N1–Co1–N3 74.27(8), N2–Co1–N3 141.13(8), Cl1–Co–Cl2 116.53(3), N1–Co1–Cl1 150.31(6), N2–Co1–Cl1 98.25(6), N1–Co1–Cl2 93.16(6), N2–Co1–Cl2 102.58(6), N3–Co1–Cl1 98.20(6), N3–Co1–Cl2 101.06(6).

electronic effect and steric hindrance of the ligand on 1,3-butadiene polymerization. As shown in Table 2, it is clear that the ligand structure, particularly the substituent at the *para*-position of the iminoaryl ring, influenced the polymerization behavior of 1,3-butadiene. For example, complexes **3d** and **3e** with electron-withdrawing substituents (R_3 = F and Cl, re-

Table 2
Polymerization of 1,3-butadiene (BD) using (α-diimine)Co(II) complex/EASC catalyst.

Entry	Complex	Yield (%)	$M_n{}^a$ (10^4)	$M_w/M_n{}^a$	Microstructure [b] (%)		
					cis-1,4	*trans*-1,4	1,2
1	**3a**	91.8	10.5	3.99	95.9	2.1	2.0
2	**3b**	91.8	10.6	4.08	96.0	2.1	1.9
3	**3c**	32.2	38.1	1.96	98.0	1.1	0.9
4	**3d**	95.7	9.0	4.11	95.4	2.4	2.2
5	**3e**	94.0	8.7	3.50	95.8	2.7	1.5
6	**3f**	91.2	9.8	3.96	95.3	2.3	2.4
7	**3g**	91.2	10.2	3.65	95.4	2.3	2.3
8	**3h**	92.7	8.9	4.18	95.5	2.1	2.4
9	**3i**	91.7	9.0	3.96	95.3	2.3	2.4
10	**3j**	93.2	9.4	3.87	94.9	2.4	2.7
11	**3k**	92.6	8.9	3.98	95.3	2.1	2.6
12	**4a**	76.3	14.4	2.57	95.9	2.4	1.7
13	$CoCl_2$	6.3	—	—	—	—	—

Polymerization conditions: [BD] = 1.85 mol/L, [BD]/[Co] = 2000, [Al]/[Co] = 50, toluene 10 ml, 30 min, 20 °C.
[a] Determined by GPC.
[b] Determined by ^1H and ^{13}C NMR.

spectively) gave higher polymer yields (95.7% and 94.0%, respectively) than unsubstituted **3a** (91.8%). **3b** with a methyl group displayed the same catalytic activity as **3a**. The lowest catalytic activity was observed in the case of **3c** with an electron-donating group (–OCH_3), with the polymer yield of 32.2%. These results can be explained by that an electron-donating group reduces the cationic nature of the metal center, which consequently weakened the coordination of the monomer to the active center, while an electron-withdrawing group reduces the electron density of the metal center, and the increased Lewis acidity facilitated the coordination between 1,3-butadiene and the Co center, leading to an increased chain propagation rate [44,49]. Thus, an electron-withdrawing substituent in the ligand of the Co complex gives a higher catalytic activity for 1,3-butadiene polymerization. On the other hand, a complex with an electron-donating group exhibited a higher *cis*-1,4 stereoselectivity than its counterpart with an electron-withdrawing group. For example, **3c** gave polybutadiene with the highest *cis*-1,4 content of 98.0% (Fig. 4), while **3d** displayed the lowest *cis*-1,4 stereoselectivity of 95.4%. This result implies that 1,3-butadiene was coordinated to the metal center with a high electronic density by the *cis*-η^4 mode rather than the *trans*-η^2 mode [34,49], which would result in the formation of the *cis*-1,4-isomer. In addition, the complex having an electron-donating group **3c** afforded polymer with a high molecular weight (M_n = 38.1 × 10^4) and narrow molecular weight distribution (M_w/M_n = 1.96), suggesting that remote electron-donating substituents can retard the chain transfer reaction to some extent [44].

In the polymerization of 1,3-diene with transition metal catalysts, both the electronic effect and steric hindrance of the substituent on the ligand influence catalytic activity and the microstructure of the polymer [42–49]. For example, we recently found that the 2,6-bis(imino)pyridyl Co(II) complex with a bulky isopropyl group at the *ortho*-position of the phenyl ring exhibited a lower catalytic activity for 1,3-butadiene polymerization and gave a polymer with a higher molecular weight and
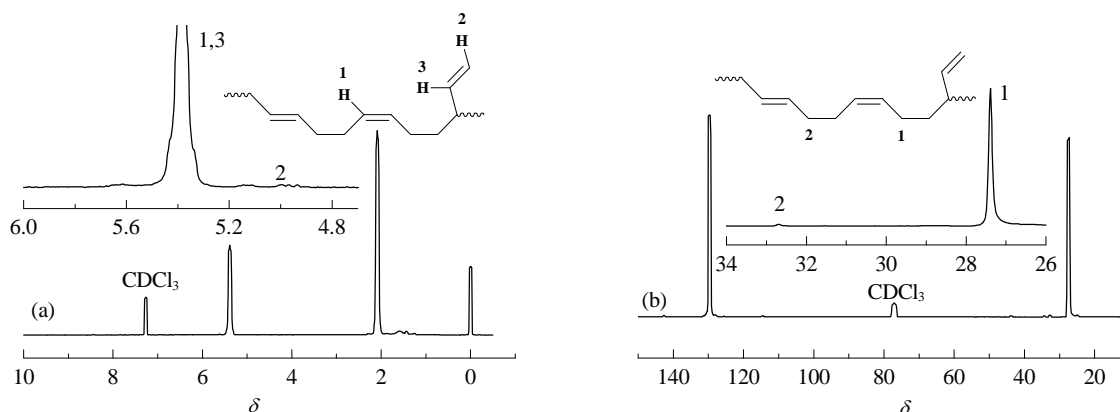
Fig. 4. NMR spectra of polybutadiene obtained with the **3c**/EASC system (entry 3 in Table 2). (a) ^{1}H NMR; (b) ^{13}C NMR.

cis-1,4 content than did the complexes bearing methyl and ethyl groups [44]. Jie et al. [49] reported that dinuclear Co(II) complexes (3-aryliminomethyl-2-hydroxybenzaldehyde Co(II)) with an isopropyl group at the *ortho*-position of the phenyl ring gave a higher polymer yield and lower molecular weight polymer than the complex having a methyl group. Therefore, the effect of the steric hindrance of substituents (methyl, ethyl, and isopropyl at 2-position (**3f–3h**) and 2,6-positions (**3i–3k**) of iminoaryl ring) on 1,3-butadiene polymerization was further investigated in this study (Table 2, entries 6–11). To our surprise, it was found that the steric hindrance of the substituents on the iminoaryl rings of α-diimine hardly influenced the catalytic behavior of the complexes. All these complexes (**3i–3k**) gave polybutadienes in high yields ranging from 91% to 93% with *cis*-1,4 contents of about 95%. This result may be due to the similar structural parameters of the cobalt complexes giving rise to the similar polymerization behavior. For example, the crystal structures of the two representative complexes **3i** and **3k** have almost the same bond distances for Co1–N1, Co1–N2, Co1–Cl1, and Co1–Cl2 and the same bond angles for N1–Co–N2 and Cl1–Co–Cl2. Moreover, both the phenyl groups of **3i** and **3k** are nearly perpendicular to the central plane [Co–N1–C1–C2–N2]. It is worth noting that cobalt complexes with the α-diimine ligands displayed a higher catalytic activity
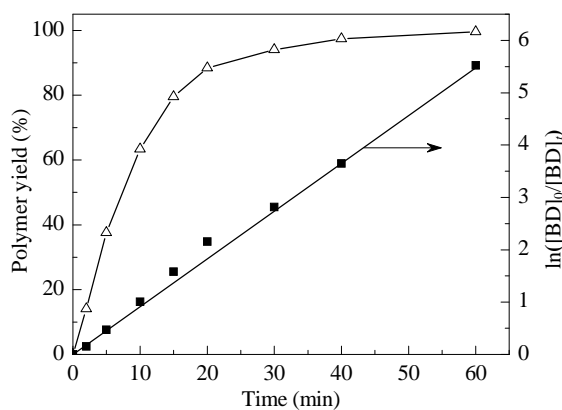
than 2,6-bis[[(2,6-diisopropylphenylimino)ethyl]pyridine CoCl₂ (**4a**), which is possibly due to their more open coordinated environment. 1,3-Butadiene polymerization conducted with the CoCl₂/EASC system under identical reaction conditions produced polybutadiene in a significantly lower yield, showing the importance of the ligand at the active center (Table 2, entry 13).

The effect of polymerization time on 1,3-butadiene polymerization catalyzed by **3e**/EASC ([Al]/[Co] = 50) was examined at 20 °C. The polymer yield versus polymerization time is depicted in Fig. 5. The polymer yield sharply increased during the early period (~15 min) of polymerization, and then it increased monotonically until 60 min, when it attained the almost complete conversion of 1,3-butadiene. The plot of $\ln[BD]_0/[BD]_t$ with polymerization time showed a good linear relationship, indicating that the polymerization rate is first order with respect to the monomer. The polymerization results are shown in Table 3. The M_n of the produced polymer increased with polymerization time, while the M_w/M_n increased from 1.93 to 4.57. The polymers produced had high stereoregularity throughout the entire polymerization.

The effects of polymerization conditions on catalytic activity and polymer microstructure were further examined using the **3e**/EASC catalyst. The type of cocatalyst, [Al]/[Co] molar ratio, and polymerization temperature affected the catalytic behavior of the catalyst. The results are summarized in Table 4. In com-

Fig. 5. Polymer yield and $\ln([BD]_0/[BD]_t)$ versus polymerization time for 1,3-butadiene polymerization catalyzed by **3e**/EASC catalyst. Polymerization conditions: [BD] = 1.85 mol/L, [BD]/[Co] = 2000, [Al]/[Co] = 50, toluene 10 ml, 20 °C.

Table 3

Effect of polymerization time on 1,3-butadiene polymerization with the **3e**/EASC catalyst.

Entry	Time (min)	Yield (%)	M_n[a] (10⁴)	M_w/M_n[a]	Microstructure[b] (%)		
					cis-1,4	*trans*-1,4	1,2
1	2	14.1	5.7	1.93	96.5	1.9	1.6
2	5	37.6	5.6	2.82	96.6	1.3	2.1
3	10	63.4	6.4	3.34	95.8	2.7	1.5
4	15	79.5	7.7	3.78	95.3	2.3	2.4
5	20	88.4	8.2	3.84	95.6	2.2	2.2
6	30	94.0	8.7	3.51	95.0	2.3	2.7
7	40	97.4	8.0	4.33	95.3	2.4	2.3
8	60	99.6	7.9	4.57	94.9	2.8	2.3

Polymerization conditions: [BD] = 1.85 mol/L, [BD]/[Co] = 2000, [Al]/[Co] = 50, toluene 10 ml, 20 °C.

[a] Determined by GPC.

[b] Determined by ^{1}H and ^{13}C NMR.

Table 4
1,3-Butadiene polymerization behavior with complex **3e** activated with aluminum cocatalyst.

Entry	Cocatalyst	[Al]/[Co]	T (°C)	Yield (%)	M_n[a] (10^4)	M_w/M_n[a]	Microstructure[b] (%) cis-1,4	trans-1,4	1,2
1	MAO	100	20	53.0	11.5	1.70	96.9	1.7	1.4
2	MAO	150	20	73.0	10.4	1.72	96.3	2.0	1.7
3	MAO	200	20	74.2	9.6	1.74	96.2	2.0	1.8
4	DEAC	50	20	75.0	2.2	2.86	86.0	8.2	5.8
5	EASC	10	20	89.2	5.6	4.02	95.3	1.8	2.9
6	EASC	20	20	91.3	8.1	4.53	95.2	2.5	2.3
7	EASC	30	20	92.8	6.6	4.56	96.0	1.2	2.8
8	EASC	70	20	100	6.9	4.74	95.3	2.1	2.6
9	EASC	100	20	100	8.7	4.12	95.7	1.9	2.4
10	EASC	50	0	68.7	19.5	2.42	98.3	0.9	0.8
11	EASC	50	20	94.0	8.7	3.51	95.8	2.7	1.5
12	EASC	50	50	100	4.2	6.47	88.2	6.6	5.2
13	EASC	50	70	96.0	2.7	7.18	79.7	11.7	8.6
14	EASC	50	90	86.7	2.5	7.59	77.3	15.2	7.5

Polymerization conditions: [BD] = 1.85 mol/L, [BD]/[Co] = 2000, toluene 10 ml, 30 min.
[a] Determined by GPC.
[b] Determined by ^{1}H and ^{13}C NMR.

bination with MAO ([Al]/[Co] = 100–200), **3e** gave polybutadienes having a high *cis*-1,4 content (more than 96%), high molecular weight (~10^5), and relatively narrow molecular weight distribution (M_w/M_n ~1.7) in a moderate polymer yield (53.0%–74.0%). **3e**/DEAC exhibited a slightly higher catalytic activity (75.0%), while the polymer produced had a lower *cis*-1,4 content of 86.0%. **3e**/EASC afforded polymer with the highest yield of 94.0% and the relatively high *cis*-1,4 content of 95.8%. It is worth noting that even at the relatively low [Al]/[Co] ratio of 10, the polymer yield was 89.2%, which is much higher than that of the 2,6-bis(benzimidazol-2-yl)-pyridine Co(II)/EASC catalyst whose polymer yields were 8.1% and 38.1% even at [Al]/[Co] ratios of 50 and 100, respectively [46]. The polymer yield increased with the [Al]/[Co] ratio, and almost complete conversion was obtained at the [Al]/[Co] ratio of 70. The influence of the [Al]/[Co] ratio on the molecular weight and molecular weight distribution of the polymers did not exhibit an obvious pattern, indicating that the chain transfer to alkylaluminum was not as significant as in the case of olefin polymerization [58,59]. The *cis*-1,4 contents of the polymers were more than 95% in the [Al]/[Co] ratio range examined.

The polymerization temperature considerably influenced catalytic activity and the microstructure of the polymers. Interestingly, the **3e**/EASC catalyst gave the polymer yield of 68.7% at the relatively low temperature of 0 °C, which is much higher than those of other Co-based catalysts reported. For instance, the 2,6-bis(benzimidazolyl)pyridines Co(II) and 3-aryliminomethyl-2-hydroxybenzaldehydes Co(II) catalyst systems only produce trace amounts of polymer [46,49], and the Co complex bearing an imino-pyridyl alcohol ligand gave a low polymer yield of 39.3% at 0 °C [48]. The catalytic activity increased with the polymerization temperature. The polymer yield was 100% when the polymerization temperature was increased to 50 °C. Although the polymerization rate would

decrease at even higher temperatures, which is common in late transition metal catalyzed polymerization, the present catalytic system showed a remarkably high catalytic activity indicated by the high polymer yield of 96.0% at 70 °C and even a high yield of 86.7% at 90 °C. The M_n of polybutadienes decreased from 19.5×10^4 to 2.5×10^4 as the temperature increased from 0 to 90 °C, along with M_w/M_n broadening from 2.42 to 7.59. These changes are due to the enhancement of chain transfer reactions with increased polymerization temperature. The microstructure of the polymers was also substantially affected by the polymerization temperature. The *cis*-1,4 content decreased as the polymerization temperature increased, while the *trans*-1,4 and 1,2 contents increased. The increased *trans*-1,4 content can be attributed to facilitated *anti-syn* isomerization at higher temperature [49], while the increase of the 1,2 content is probably due to that the new coming monomer inserts at the C_3 of the η^3-allyl group formed at the active site more easily at higher temperature, leading to 1,2-isomer formation [60].

4. Conclusions

A series of Co(II) complexes with α-diimine (**2a–2k**) ligands were synthesized and characterized. The representative complexes **3i** and **3k** adopted a deformed tetrahedron configuration comprising two Cl atoms and two N atoms of the ligand, which was shown by single crystal X-ray analysis. After activation by EASC, all the complexes **3a–3k** gave polybutadienes with high *cis*-1,4 contents (up to 98%) in high polymer yields. Complexes **3c** and **3d** with electron-drawing groups (F and Cl, respectively) on the iminoaryl ring exhibited a higher catalytic activity but lower stereoselectivity than **3b** and **3c** with electron-contributing groups (methyl and methoxyl, respectively). The steric hindrance of the substituents on the iminoaryl rings did not influence catalytic activity, or the molecular weight, molecular weight distribution, and microstructure of the polymers. The catalytic activity of **3e** activated with different alkylaluminum cocatalysts was in the order EASC > DEAC > MAO. An increase of the [Al]/[Co] ratio enhanced catalytic activity, while the *cis*-1,4 content of the polymer remained almost unchanged. The microstructure of the polymers was considerably affected by the polymerization temperature, and the *cis*-1,4 content decreased as the polymerization temperature increased, while the *trans*-1,4 and 1,2 contents increased.

References

[1] Ricci G, Sommazzi A, Masi F, Ricci M, Boglia A, Leone G. *Coord Chem Rev*, 2010, 254: 661
[2] Shen Z Q. *Inorg Chim Acta* (沈之荃. 无机化学学报), 1987, 140: 7
[3] Friebe L, Nuyken O, Obrecht W. *Adv Polym Sci*, 2006, 204: 1
[4] Fischbach A, Anwander R. *Adv Polym Sci*, 2006, 204: 155
[5] Pan L, Zhang K Y, Nishiura M, Hou Z M. *Angew Chem Int Ed*, 2011, 50: 12012
[6] Du G X, Wei Y L, Ai L, Chen Y Y, Xu Q, Liu X A, Zhang S W, Hou Z M, Li X F. *Organometallics*, 2011, 30: 160
[7] Nishiura M, Hou Z M. *Nat Chem*, 2010, 2: 257
[8] Thiele S K H, Wilson D R. *J Macromol Sci, Polym Rev*, 2003, C43: 581

[9] Miyazawa A, Kase T, Hashimoto K, Choi J C, Sakakura T, Ji Z J. *Macromolecules*, 2004, 37: 8840

[10] Meppelder G J M, Fan H T, Spaniol T P, Okuda J. *Inorg Chem*, 2009, 48: 7378

[11] Qiao Y L, Zhu H, Wu Y X, Wang J, Xu R W, Wu G Y, Yang W T. *Acta Polym Sin* (乔雨露, 朱寒, 吴一弦, 王金, 徐日炜, 武冠英, 杨万泰. 高分子学报), 2010: 640

[12] Gong D R, Wang B L, Bai C X, Bi J F, Wang F, Dong W M, Zhang X Q, Jiang L S. *Polymer*, 2009, 50: 6259

[13] Appukuttan V, Zhang L, Ha C S, Kim I. *Polymer*, 2009, 50: 1150

[14] Gao W, Cui D M. *J Am Chem Soc*, 2008, 130: 4984

[15] Kaita S, Hou Z M, Wakatsuki Y. *Macromolecules*, 1999, 32: 9078

[16] Zhang L X, Suzuki T, Luo Y, Nishiura M, Hou Z M. *Angew Chem Int Ed*, 2007, 46: 1909

[17] Arndt S, Beckerle K, Zeimentz P M, Spaniol T P, Okuda J. *Angew Chem Int Ed*, 2005, 44: 7473

[18] Kaita S, Yamanaka M, Horiuchi A C, Wakatsuki Y. *Macromolecules*, 2006, 39: 1359

[19] Kaita S, Hou Z M, Wakatsuki Y. *Macromolecules*, 2001, 34: 1539

[20] Fischbach A, Meermann C, Eickerling G, Scherer W, Anwander R. *Macromolecules*, 2006, 39: 6811

[21] Evans W J, Giarikos D G, Ziller J W. *Organometallics*, 2001, 20: 5751

[22] Wang D, Li S H, Liu X L, Gao W, Cui D M. *Organometallics*, 2008, 27: 6531

[23] Colamarco E, Milione S, Cuomo C, Grassi A. *Macromol Rapid Commun*, 2004, 25: 450

[24] Nakayama Y, Baba Y, Yasuda H, Kawakita K, Ueyama N. *Macromolecules*, 2003, 36: 7953

[25] Cariou R, Chirinos J, Gibson V C, Jacobsen G, Tomov A K, Elsegood M R J. *Macromolecules*, 2009, 42: 1443

[26] Ricci G, Forni A, Boglia A, Sommazzi A, Masi F. *J Organomet Chem*, 2005, 690: 1845

[27] Ricci G, Forni A, Boglia A, Motta T, Zannoni G, Canetti M, Bertini F. *Macromolecules*, 2005, 38: 1064

[28] Ricci G, Forni A, Boglia A, Sonzogni M. *Organometallics*, 2004, 23: 3727

[29] Hu Y M, Dong W M, Jiang L S, Zhang X Q, Yu G, Cao L H. *Chin J Catal* (胡雁鸣, 董为民, 姜连升, 张学全, 郭玉, 曹丽辉. 催化学报), 2004, 25: 664

[30] Gong D R, Dong W M, Hu Y M, Bi J F, Zhang X Q, Jiang L S. *Polymer*, 2009, 50: 5980

[31] Lu J, Hu Y M, Zhang X Q, Bi J F, Dong W M, Jiang L S, Huang B T. *J Appl Polym Sci*, 2006, 100: 4265

[32] Jang Y C, Kim P, Lee H. *Macromolecules*, 2002, 35: 1477

[33] Cai Z G, Shinzawa M, Nakayama Y, Shiono T. *Macromolecules*, 2009, 42: 7642

[34] Cariou R, Chirinos J J, Gibson V C, Jacobsen G, Tomov A K, Britovsek G J P, White A J P. *Dalton Trans*, 2010, 39: 9039

[35] Furukawa J. *Pure Appl Chem*, 1975, 42: 495

[36] Cooper W. *Ind Eng Chem Prod Res Devel*, 1970, 9: 457

[37] Smirnova L V, Yatsenko L A, Boldyrev A G, Panasyuk S L, Kropacheva Y N. *Vysokomol Soedin A*, 1991, 33: 1905

[38] Oehme A, Gebauer U, Gehrke K, Lechner M D. *Angew Makromol Chem*, 1996, 235: 121

[39] Nath D C D, Shiono T, Ikeda T. *Macromol Chem Phys*, 2002, 203: 1171

[40] Sharaev O K, Kostitsyna N N, Glebova N N, Bondarenko G N, Yakovlev V A. *Polym Sci Ser B*, 2006, 48: 274

[41] Nath D C D, Shiono T, Ikeda T. *Macromol Chem Phys*, 2003, 204: 2017

[42] Endo K, Kitagawa T, Nakatani K. *J Polym Sci Part A*, 2006, 44: 4088

[43] Chandran D, Kwak C H, Ha C S, Kim I. *Catal Today*, 2008, 131: 505

[44] Gong D R, Wang B L, Cai H G, Zhang X Q, Jiang L S. *J Organomet Chem*, 2011, 696: 1584

[45] Gong D R, Jia X Y, Wang B L, Zhang X Q, Jiang L S. *J Organomet Chem*, 2012, 702: 10

[46] Appukuttan V, Zhang L, Ha J Y, Chandran D, Bahuleyan B K, Ha C S, Kim I. *J Mol Catal A*, 2010, 325: 84

[47] Nobbs J D, Tomov A K, Cariou R, Gibson V C, White A J P, Britovsek G J P. *Dalton Trans*, 2012, 41: 5949

[48] Ai P F, Chen L, Guo Y T, Jie S Y, Li B G. *J Organomet Chem*, 2012, 705: 51

[49] Jie S Y, Ai P F, Li B G. *Dalton Trans*, 2011, 40: 10975

[50] Johnson L K, Killian C M, Brookhart M. *J Am Chem Soc*, 1995, 117: 6414

[51] Killian C M, Johnson L K, Brookhart M. *Organometallics*, 1997, 16: 2005

Graphical Abstract

Chin. J. Catal., 2013, 34: 1560–1569   doi: 10.1016/S1872-2067(12)60625-1

Highly active and *cis*-1,4 selective polymerization of 1,3-butadiene catalyzed by cobalt(II) complexes bearing α-diimine ligands

Xiangyu Jia, Heng Liu, Yanming Hu *, Quanquan Dai, Jifu Bi, Chenxi Bai, Xuequan Zhang *
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; University of Chinese Academy of Sciences; Dalian University of Technology

cis-1,4-polybutadiene yield 32.2%–95.7%
Content up to 98.0%
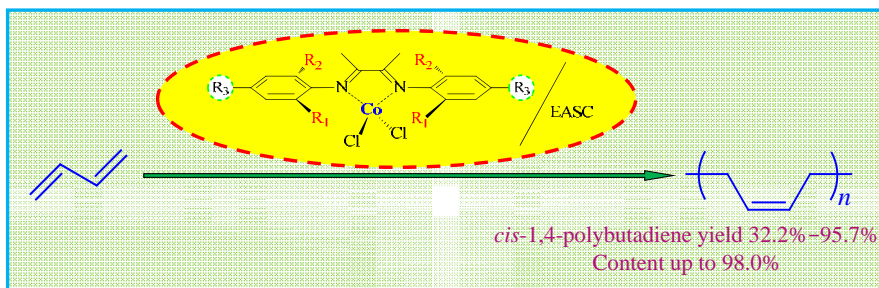
A series of cobalt(II) complexes ligated by α-diimine have been synthesized and characterized. The catalyst system [α-diimine]CoCl$_2$/EASC shows high catalytic activity and *cis*-1,4 selectivity (up to 98%) for 1,3-butadiene polymerization.

[52] Svejda S A, Brookhart M. *Organometallics*, 1999, 18: 65
[53] Elgert K F, Quack G, Stutzel B. *Polymer*, 1974, 15: 612
[54] Elgert K F, Quack G, Stutzel B. *Polymer*, 1975, 16: 154
[55] Chung C K, Grubbs R H. *Org Lett*, 2008, 10: 2693
[56] Dieck H T, Svoboda M, Greiser T. *Z Naturforsch B*, 1981, 36: 823
[57] Pesch J, Harms K, Bach T. *Eur J Org Chem*, 2004*:* 2025
[58] Quintanilla E, Di Lena F, Chen P. *Chem Commun*, 2006: 4309
[59] Quevedo-Sanchez B, Nimmons J F, Coughlin E B, Henson M A. *Macromolecules*, 2006, 39: 4306
[60] Porri L, Giarrusso A, Ricci G. *Prog Polym Sci*, 1991, 16: 405

α-二亚胺钴配合物催化1,3-丁二烯高活性与高顺式-1,4选择性聚合

贾翔宇[a,b], 刘　恒[a,b], 胡雁鸣[c,#], 代全权[a], 毕吉福[a], 白晨曦[a], 张学全[a,*]

[a]中国科学院长春应用化学研究所高性能合成橡胶工程技术中心,吉林长春130012
[b]中国科学院大学, 北京100049
[c]大连理工大学化工学院高分子科学与工程系, 辽宁大连116012

摘要: 合成了一系列α-二亚胺钴配合物[ArN=C(Me)–(Me)C=NAr]CoCl$_2$ (Ar = C$_6$H$_5$, **3a**; 4-MeC$_6$H$_4$, **3b**; 4-MeOC$_6$H$_4$, **3c**; 4-FC$_6$H$_4$, **3d**; 4-ClC$_6$H$_4$, **3e**; 2-MeC$_6$H$_4$, **3f**; 2-EtC$_6$H$_4$, **3g**; 2-^{i}PrC$_6$H$_4$, **3h**; 2,4,6-Me$_3$C$_6$H$_2$, **3i**; 2,6-Et$_2$C$_6$H$_3$, **3j**; 2,6-^{i}PrC$_6$H$_3$, **3k**)和作为对比的吡啶双亚胺二氯化钴配合物(**4a**),并用X射线单晶衍射方法研究了配合物**3i**, **3k**和**4a**的分子结构. α-二亚胺钴配合物在倍半乙基氯化铝的作用下对丁二烯聚合有较高的催化活性,得到的顺式-1,4结构含量达98%,且有较高分子量($M_n \approx 1\times10^4$–1×10^5)的聚丁二烯. 配体的电子效应影响催化剂的活性及顺式-1,4选择性,而配体的空间位阻对丁二烯聚合几乎没有影响. 详细研究了聚合时间、聚合温度、烷基铝助催化剂及铝比等条件对丁二烯聚合行为的影响.
关键词: 钴; α-二亚胺; 1,3-丁二烯; 聚丁二烯; 聚合