



Stereospecific polymerizations of 1,3-butadiene catalyzed by Co(II) complexes ligated by 2,6-bis(benzimidazolyl)pyridines

Vinukrishnan Appukkuttan, Lin Zhang, Ju Young Ha, Deepak Chandran, Bijal Kottukkal Bahuleyan, Chang-Sik Ha, Il Kim*

The WCU Center for Synthetic Polymer Bioconjugate Hybrid Materials, Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

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ABSTRACT

The tridentate 2,6-bis(benzimidazolyl)pyridine ligands were combined with CoCl_2 to prepare a series of complexes of the general formula: $[\text{Py}(\text{Bm-R})_2]\text{CoCl}_2$ (where Py = pyridyl, Bm = benzimidazolyl, R = H (**3a**); –Me (**3b**); –Bz (**3c**)). These complexes were characterized by mass and elemental analysis, along with X-ray diffraction analysis. The geometry around the five coordinated Co atom in **3c** consists of a distorted square pyramid in which cobalt is surrounded by tridentate $\text{N}\ddot{\text{N}}\ddot{\text{N}}$ ligand and two chlorines. The Co(II) complexes exhibited high catalytic activities for the polymerization of 1,3-butadiene on activation with alkylaluminums to yield predominantly *cis*-1,4-polybutadiene with high molecular weight. Choice of cocatalysts was found to be a decisive factor in determining the activity and product microstructure. Ethylaluminum sesquichloride (EASC) was found to be the most efficient one resulting in polymers with about 97% 1,4-*cis* content. The ligand modification by N-alkylation shows considerable influence on the catalytic activity by virtue of variation of electronic environment of the active centers. The stereoselectivity of the catalysts was consistent for a wide range of reaction conditions, except the formation of a considerable amount of 1,4-*trans* inserted units at high temperature.

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1. Introduction

The catalytic insertion polymerization of 1,3-butadiene (BD) by transition metals is characterized by the high degree of regioselectivity of the incoming monomer and also by the extend of stereoregulation of the formed polybutadiene (PBD) resulting in polymers of different isomeric forms, such as *cis*-1,4, *trans*-1,4, 1,2-syndiotactic, 1,2-isotactic, and 1,2-atactic. The use of different catalysts produces PBDs with different micro and macro structures making the properties and processability different and hence finding distinctive applications [1,2]. Selective *cis*-1,4 polymerization of BD is of prime importance since the elastomeric rubbery product, *cis*-1,4-PBD, constitutes as one of the major ingredients in the tire industry [1]. Industrially, Ziegler–Natta catalysts of Ti and, carboxylates, acetylacetonates or alcoholates of transition metals in combination with various organoaluminums are used in the production of *cis*-1,4-PBDs [1–3]. Cobalt based catalysts attract special interest as the product microstructure depends on catalyst formulation [4]. The carboxylates and halides of Co are stereoselective to high *cis*-1,4-PBDs when activated with methylalumoxane (MAO) [5,6]. However,

the Co halides when combined with triphenyl phosphine and pyridyl adducts produced predominantly 1,2-PBD [7] and even produced highly *trans*-1,4-PBD when triethyl amine adduct was used [8].

The structure of active center is the determining factor for the activity, molecular weight (MW) and more importantly the stereochemistry of the polymerization. For this reason, recent interests are vested on organometallic single-site homogeneous catalyst comprising of transition metals and lanthanides with tailored catalyst design for the production of highly stereoregular PBDs [1,2,9–14]. Over the past decade, after the introduction of 2,6-bis(imino)pyridine ligand for cobalt and iron catalysts, a large extend of $\text{N}\ddot{\text{N}}\ddot{\text{N}}$ tridentate ligands based on either derivatives of bis(imino)pyridines or through designing new organic compounds especially consisting of heterocyclics are reported [15–18]. Though such complexes were extensively studied for the oligo- and polymerization of olefins, their extension as catalysts in diolefin polymerization is very few in number. However, the significance of the ligand environment towards the polymer microstructure and activity were revealed by previous reports involving Co(II) catalysts based on $\text{N}\ddot{\text{N}}\ddot{\text{N}}$ [19–22] and $\text{N}\ddot{\text{O}}$ [23,24] chelates, which produces high *cis*-1,4-PBDs. It could be observed from these systems that the steric bulkiness of substituents adjacent to metal center imparted a negative influence towards the polymerization activity and on molecular weight (MW) of resulting polymers.

* Corresponding author. Tel.: +82 51 510 2399; fax: +82 51 513 7720.
E-mail address: ilkim@pusan.ac.kr (I. Kim).

In order to get deeper insights on this effect, in the present study, we are utilizing the open chelating site of 2,6-bis(benzimidazolyl)pyridines devoid of any adjacent substituents as a tridentate ligand for Co complexes in the production of *cis*-1,4-PBDs. Even though the transition metal complexes based on such ligands were reported previously to study structure–property relation [25–27], much attention was not diverted to exploit their potential as coordination catalysts. Chromium complexes of similar ligand systems were reported to produce oligomers and polymers of ethylene simultaneously [28,29]. As the continuation of the study in search for new catalysts for BD polymerization, herein we report the synthesis, characterization and BD polymerization aspects of 2,6-bis(benzimidazolyl)pyridine ligated tridentate Co(II) complexes. The complexes were synthesized in high yields and their structure was confirmed by mass and elemental analyses. The crystal structure was also elucidated by single crystal X-ray diffraction technique. BD polymerization has been performed at different reaction conditions to evaluate their influence on the catalytic activity and the microstructure of polymers. In a commercial point of view, the effectiveness of ethylaluminum sesquichloride (EASC) as a cheaper and efficient cocatalyst has also been explored.

2. Experimental

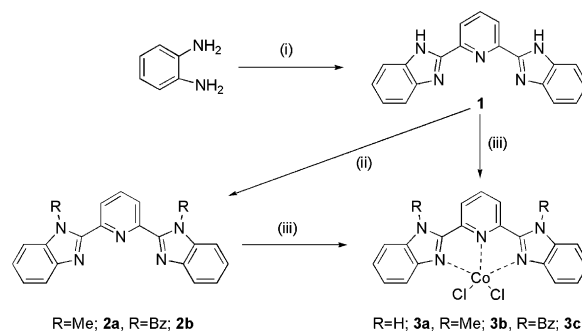
2.1. General procedures and materials

Reactions involving air or moisture sensitive compounds were performed under a purified nitrogen atmosphere using Schlenk technique. Toluene was distilled over Na/benzophenone and stored over molecular sieves (4 Å). Polymerization grade BD (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX™ catalyst and molecular sieve 5 Å/13×. Alkylaluminums such as MAO, ethylaluminum sesquichloride (EASC), methylaluminum dichloride (MADC) and diethylaluminum chloride (DEAC), all in a toluene solution, were obtained from Aldrich and used without further purification. All other chemicals were obtained from Aldrich and used without further purification unless otherwise mentioned.

Elemental analysis of metal complexes was carried out using Vario EL analyzer. Fast atom bombardment mass spectroscopy (FAB-MS) was determined using JMS-700, JEOL instrument. The experimental detail of single crystal analysis is as follows. The crystal was picked up with Paratone N oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source and a nitrogen cold stream (-100 °C). The data were corrected for Lorentz and polarization effects (SAINT), and semiempirical absorption corrections based on equivalent reflections were applied (SADABS). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL). All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. The crystal data for **3c** has been deposited at Cambridge Crystallographic Data Center with number CCDC 747967. The data can be obtained free of charge from the Cambridge Crystallographic Data Center through http://www.ccdc.cam.ac.uk/data_request/cif.

2.2. Synthesis of ligands (Scheme 1)

The syntheses of ligands and Co(II) complexes are summarized in Scheme 1. The 2,6-bis(benzimidazolyl)pyridine ligands, **1**, **2a** and **2b** were prepared according to the reported procedures [27,29].



Scheme 1. Synthesis of complexes: (i) pyridine-2,6 dicarboxylic acid, (ii) NaH/R-X (Me-I, Bz-Br) and (iii) CoCl₂·6H₂O.

2.3. Synthesis of cobalt complexes (**3a–3c**)

2.3.1. 2,6-Bis(benzimidazol-2-yl)-pyridine cobalt(II) chloride (**3a**)

A mixture of **1** (0.60 g, 1.93 mmol) and CoCl₂·6H₂O (0.46 g, 1.93 mmol) was stirred in 10 mL of THF for 12 h at room temperature. The green colored solid precipitated was filtered, washed with THF (3 × 20 mL) and once with diethyl ether (20 mL), and then dried under vacuum. Yield 0.74 g (87%). Elemental analysis for C₁₉H₁₃N₅CoCl₂, calcd: C 51.73, H 2.97, N 15.87 found: C 51.26, H 3.01, N 15.76. FAB-MS (m/z): 405 [M–Cl]⁺.

2.3.2. 2,6-Bis(1'-methylbenzimidazol-2'-yl)pyridine cobalt(II) chloride (**3b**)

Procedure similar for **3a** was adopted, compound **2b** (0.50 g, 1.47 mmol) and CoCl₂·6H₂O (0.35 g, 1.47 mmol) yielding 0.62 g (90%) of green solid. Elemental analysis for C₂₁H₁₇N₅CoCl₂, calcd: C 53.75, H 3.65, N 14.93 found: C 53.32, H 3.71, N 15.12. FAB-MS (m/z): 436 [M–Cl]⁺.

2.3.3. 2,6-Bis(1'-benzylbenzimidazol-2'-yl)pyridine cobalt(II) chloride (**3c**)

Procedure similar for **3a** was adopted, compound **2c** (0.50 g, 1.01 mmol) and CoCl₂·6H₂O (0.24 g, 1.01 mmol) yielding 0.55 g (88%) of green solid. Elemental analysis for C₃₃H₂₅N₅CoCl₂, calcd: C 63.78, H 4.05, N 11.27 found: C 64.17, H 4.10, N 11.32. FAB-MS (m/z): 587 [M–Cl]⁺.

2.4. Polymerization procedure

Solution polymerizations of BD in toluene were carried out in a glass reactor (40 mL) connected with a vacuum line. A typical polymerization procedure is as follows. 2.5 μmol of the precatalyst **3a** was dissolved in 19.45 mL of toluene. After regulating the temperature of reaction mixture to 30 °C, 0.757 g of BD (to make 0.7 M solution) was equilibrated to toluene. The polymerization started by injecting 0.55 mL of EASC (Al/Co = 400) to the solution. For the facile agitation of the reaction mixture by preventing a sharp increase of viscosity due to high yield and possible crosslink reactions, the polymerization time was controlled to 10 min. The resulting solution mixture was poured into acidified methanol (100 mL of a 5% (v/v) solution of HCl) containing butylhydroxytoluene as stabilizer. The precipitated polymer was isolated by filtration, washed with methanol, and then dried overnight at 50 °C under vacuum. Polymer yield was determined by gravimetry.

2.5. Polymer characterization

Molecular weight (MW) and molecular weight distribution (MWD) of PBDs were determined by gel permeation chromatography (GPC) using a Waters 2414 series system fitted with a refractive

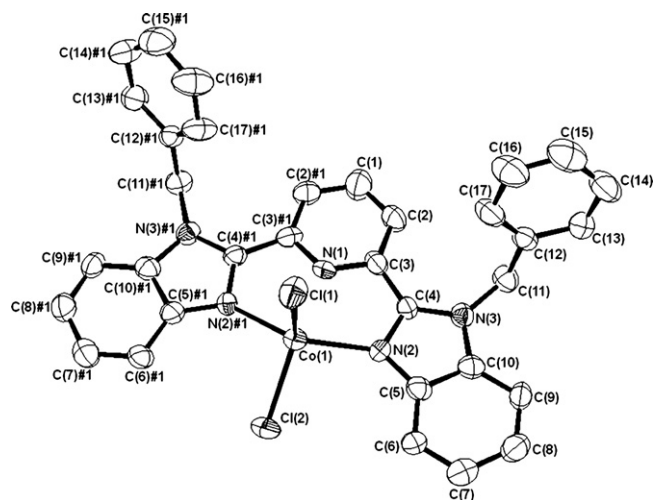


Fig. 1. ORTEP representation of complex **3c** with 50% thermal ellipsoids. Hydrogen atoms and oxygen atoms from water molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–N(2) 2.108(6), Co(1)–N(2)#1 2.108(6), Co(1)–N(1) 2.161(9), Co(1)–Cl(2) 2.283(4), Co(1)–Cl(1) 2.324(3), N(2)–C(4) 1.339(10), N(2)–C(5) 1.381(10); N(2)–Co(1)–N(2)#1 144.5(4), N(2)–Co(1)–N(1) 74.39(19), N(2)–Co(1)–Cl(2) 101.03(19), N(1)–Co(1)–Cl(2) 156.9(3), N(2)–Co(1)–Cl(1) 99.19(18), N(1)–Co(1)–Cl(1) 93.5(3), Cl(2)–Co(1)–Cl(1).

index detector in THF at 25 °C calibrated by polystyrene standards. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded at 25 °C on a Varian Gemini 2000 spectrometer in CDCl₃ containing tetramethylsilane as standard. All chemical shifts are reported in parts per million (ppm). The typical NMR chemical shifts for PBDs are as follows: ¹H NMR: δ = 4.8–5.2 (=CH₂ of 1,2-BD unit), 5.2–5.8 (–CH of 1,4-BD unit and –CH of 1,2-BD unit), ¹³C NMR: δ = 27.4 (1,4-*cis* BD unit), 32.7 (1,4-*trans* BD unit), 127.7–131.8 (1,4-BD unit), 113.8–114.8 and 143.3–144.7 (1,2-BD unit).

3. Results and discussion

3.1. Synthesis and characterization of cobalt complexes

The 2,6-bis(benzimidazolyl)pyridine ligand **1** was prepared by a condensation reaction of 1,2-phenylenediamine and pyridine-2,6 dicarboxylic acid. The ligands **2a** and **2b** were obtained in high yields by N-alkylation with corresponding alkyl halides through sodium salts of **1** [27,29]. Cobalt complexes **3a–3c** were prepared in good yields by the treatment of corresponding ligands with 1 equiv. of CoCl₂·6H₂O in THF at room temperature (Scheme 1). The green colored cobalt complexes were consistent with their elemental and FAB-Mass analyses.

Single crystals of complex **3c** suitable for X-ray diffraction analysis were obtained from slow evaporation from a methanolic solution. The molecular structure and selected bond lengths and angles of **3c** are shown in Fig. 1 (see Supplementary data for detailed crystallographic information). The geometry around the five coordinated cobalt atom in **3c** consists of a distorted square pyramid in which cobalt is surrounded by tridentate NN'N' ligand and two chlorines. The equatorial plane is formed by the three nitrogen atoms from bis(benzimidazolyl) ligand and one chlorine atom, and the axial position is occupied by the second chlorine atom. The cobalt atom is deviated from the equatorial plane by 0.429 Å. The molecule has a plane of symmetry consisting of cobalt metal center, two chlorines, N (pyridyl) and C (pyridyl) (the symmetrical atoms in Fig. 1 are numbered with identical numerals preceded by # sign). The two Co–N (benzimidazole) bonds are of identical bond length (Co(1)–N(2) and Co(1)–N(2)#1 2.108 Å) and are shorter than the Co–N (pyridyl) bond (Co(1)–N(1) 2.161 Å (9)) by 0.053 Å.

The bond distance from cobalt atom to the basal chlorine atom (Co(1)–Cl(2) 2.283 Å (4)) is shorter than that of the apical chlorine atom (Co(1)–Cl(1) 2.324 Å (3)). The imidazole linkages have formal double bond character, N(2)–C(4) 1.339 Å (10). The ligand in molecular structure of the complex could be viewed as virtually planar, consisting of two benzimidazole rings and a pyridine ring. The benzimidazole rings makes a dihedral angle of 5.13° with the plane consisting of pyridine ring, whereas the benzimidazole rings are inclined by an angle of 1.04° between them. The phenyl rings are inclined away from the benzimidazole along the apex of the square pyramid in which N(3)–C(11)–C(12) bond angle is 114.2(6)°.

3.2. Effect of catalyst structure on solution polymerization of BD

The catalysts were tested for solution polymerization of BD employing toluene as a solvent. The polymerization time was limited to 10 min, keeping overall yield less than about 70%, for a facile agitation to minimize the possibility of a network formation. The polymerization results obtained by cobalt complexes **3a–3c** in combination with various alkylaluminums are summarized in Table 1. The variation of electronic nature of the complexes through the incorporation of alkyl groups on the N atom of the imidazole influenced the polymerization behavior significantly. Employing EASC as a cocatalyst, **3a** with free –NH group is more active than the methylated **3b** and the activity of benzylated **3c** is in between them (Table 1, Entries 1–3). During the activation with EASC, the –NH groups present on the complex can be deprotonated to yield an anionic amide ligand. This anionic amide ligand is in the form of an ion pair (N-anion and Al-cation) or in the free form, resulting in higher polymerization activity [29]. The lower activity of **3b**/EASC catalyst might be explained by the electron donating effect of methyl group which can possibly reduce the cationic nature of metal center resulting in a weaker coordination of monomer. In **3c**/EASC catalyst, the aryl rings delocalize the electron on ligand making the metal center more electropositive and hence a better activity. Similar electronic effects of N-alkylation were observed in our previous report involving bis(benzimidazolyl)amine cobalt complexes [24]. On comparing the BD polymerization nature of cobalt catalysts based on 2,6-bis(imino)pyridines [19,22], the present catalyst system was found to be more active probably due to the presence of a wide opened active site formed by a planar ligand structure with no adjacent substituents.

The stereochemistry of the polymerization process was followed by the microstructural analysis of polymers by NMR spectroscopy [6,30]. Figs. 2 and 3 shows ¹H NMR and ¹³C NMR spectra, respectively, of a representative PBD sample obtained by **3a**/EASC catalyst system (Entry 1 in Table 1). The catalysts with different ligand structure showed almost identical stereoselectivity with the formation of about 97% of *cis* content when activated with EASC, indicating the formation of identical active centers and the structural variation imparted only electronic perturbation on active center (*vide supra*). All the catalyst with different ligand structure produced polymers with high *M_w*s having distribution in the range 2.06–2.35 with EASC as cocatalyst. The effect of complex structure on *M_w* was not so conspicuous, demonstrating the chain transfer and/or termination reactions occur in similar way for all catalysts combined with the same cocatalyst.

In transition metal catalyzed polymerization process, the cocatalyst plays a very important role. The active species present in the polymerization process is established as cation–anion ion pair formed through the activation of catalyst precursors by the cocatalyst. The polymerization activity, molecular weight, stereoregulation, and chain transfer pathways are intimately connected with the nature of the ion pairing [31]. Thus a judicious selection of cocatalyst is of prime importance in designing the product

Table 1

Polymerizations of 1,3-butadiene over various cobalt complexes of the general formula: $[\text{Py}(\text{Bm-R})_2]\text{CoCl}_2$, Py = pyridyl, Bm = benzimidazolyl, **3a** (R = H); **3b** (R = $-\text{CH}_3$); **3c** (R = $-\text{CH}_2\text{C}_6\text{H}_5$) combined with various organoaluminum cocatalysts^a.

Entry	Cat.	Cocat. ^b	Yield (%)	M_n^c ($\times 10^{-5}$)	M_w/M_n^c	Microstructure (%) ^d		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-
1	3a	EASC	55.1	1.75	2.35	96.6	1.7	1.7
2	3b	EASC	39.7	2.12	2.06	94.7	2.1	3.2
3	3c	EASC	45.1	2.03	2.27	95.8	1.9	2.3
4	3a	MAO	3.1	0.50	1.50	95.1	3.8	1.1
5	3a	MADC	Trace	–	–	–	–	–
6	3a	DEAC	21.1	0.17	1.51	79.3	13.6	7.1

^a Polymerization conditions: catalyst = 2.5 μmol , $[\text{Al}]/[\text{Co}] = 400$, $[\text{BD}] = 0.7 \text{ M}$, total reaction volume including toluene = 20 mL, time = 10 min, and temperature = 30 °C.

^b Organoaluminum cocatalysts: EASC = ethylaluminum sesquichloride; MAO = methylaluminoxane; MADC = methylaluminum dichloride; and DEAC = diethylaluminum chloride.

^c Measured by GPC.

^d Measured by ^1H and ^{13}C NMR spectroscopies.

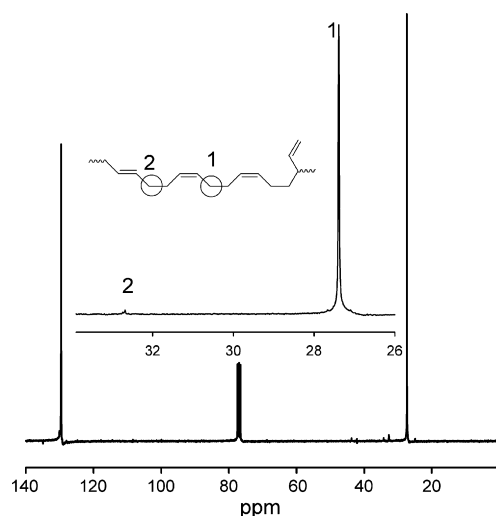


Fig. 2. ^1H NMR spectrum of the polybutadiene (Entry 1 in Table 1) synthesized by 2,6-bis(benzimidazol-2-yl)-pyridine Co(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst.

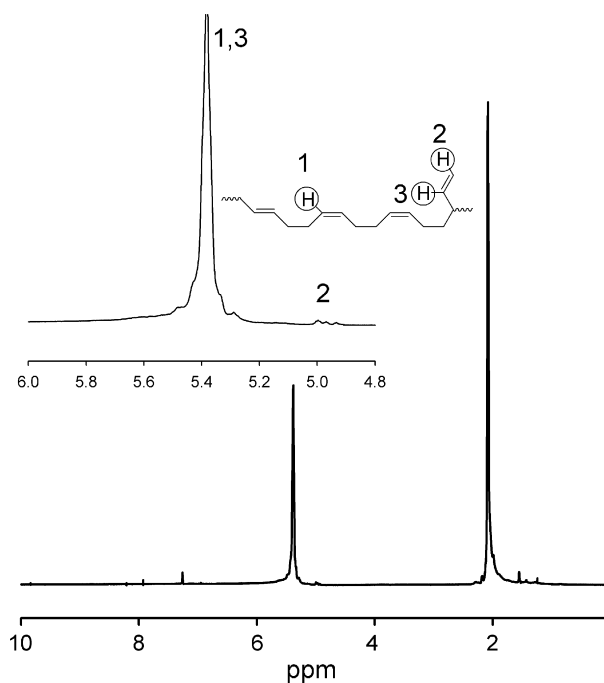


Fig. 3. ^{13}C NMR spectrum of the polybutadiene (Entry 1 in Table 1) synthesized by 2,6-bis(benzimidazol-2-yl)-pyridine Co(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst.

architecture. To evaluate the influence of the catalyst structure, BD polymerizations were done employing different cocatalysts. Among cocatalysts chosen, EASC is the most efficient one, and **3a**/EASC catalyst produced PBD with a conversion of 55.1%. The effectiveness of the other cocatalysts combined with **3a** complex decreases in the order of DEAC (21.1%) > MAO (3.2%) > MADC (trace). Since the active species exist as ion pairs, relatively smaller size of DEAC and MADC might make the ion pair much tighter, resulting in lower or negligible activity. But choice of cocatalyst significantly affected MW of polymers, **3a**/DEAC and **3a**/MAO catalysts produced polymer with much lower MW than **3a**/EASC possibly due to structural change of actual catalytic species imparted by different co activators. The PBDs produced through **3a**/MAO catalyst was found to have similar microstructure with that of **3a**/EASC, while **3a**/DEAC produces polymers with significantly higher contents *trans* (13.6) and 1,2-inserted isomer (7.1) and consequently much lower amount of *cis* isomer (79.3%).

The mechanism involving the polymerization of conjugated diolefin is more complicatedly diverse and perplexing than that of α -olefin. Regardless of central atom, an almost identical polymerization mechanism has been proposed for nearby all catalytically active species [1,2,32]. In our previous reports involving cobalt complexes, we have discussed the possible reaction pathways involving in the *cis* stereoregulation by Co metal center [20,24]. Polymerization results indicate operation of similar reaction modes in the present catalyst system. The spatial arrangement of Co orbital and energetics favors a *cis*- η^4 mode of coordination with incoming BD monomer [33]. This monomer inserts into the growing chain forming η^3 -allyl coordinated terminal group which takes preferably an *anti*-conformation which in turn leads to *cis* stereoregulated growing polymer chain. The *anti*-conformer could also isomerize to a thermodynamically more stable *syn* and consequently forming *trans* product. Recent experimental and theoretical studies of Ni and Co catalysts inferred the existence of back-biting coordination of the double bond of the penultimate inserted monomer of growing polymer chain. This makes the *anti*-*syn* isomerization energetically demanding as it involves conformational rearrangement of the last monomeric unit of the polymer chain, making the process highly *cis* stereoselective [34,35]. But in the case of DEAC due to the increased formation of *trans*- and 1,2-inserted isomers probably due to a different active center in relation with **3a**/EASC coupled with a lower kinetics favoring the thermodynamic product.

3.3. Kinetics aspects of BD polymerization

The kinetic profile was examined by performing a series of BD polymerizations using **3a**/EASC catalyst system ($[\text{Al}]/[\text{Co}] = 400$) at 30 °C. The plot of polymer yield with polymerization time is depicted in Fig. 4. The polymerization rate increases very fast in

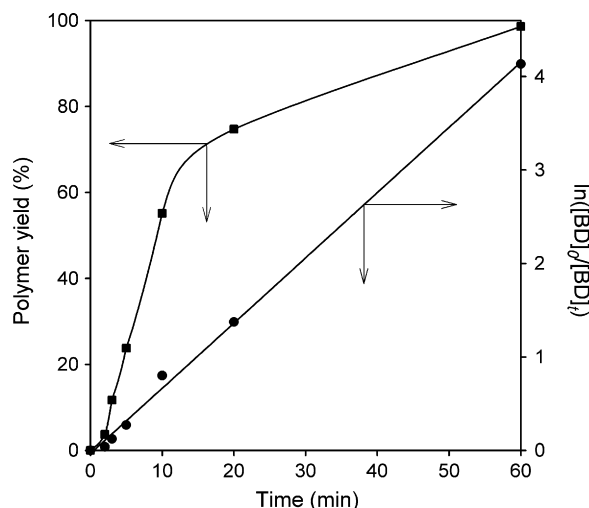


Fig. 4. The plots of polymer yield (■) and $\ln[BD]_0/[BD]_t$ (●) against polymerization time for BD polymerization by 2,6-bis(benzimidazol-2-yl)-pyridine Co(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst. Polymerization conditions: catalyst = 2.5 μmol , $[Al]/[Co] = 400$, $[BD] = 0.7\text{ M}$, total reaction volume including toluene = 20 mL, temperature = 30 °C.

the initial stages of polymerization (~10 min) and then gradually to 60 min, achieving almost complete conversion of BD. A good linear relationship in the plots, $\ln[BD]_0/[BD]_t$ versus polymerization time, where $[BD]_0$ and $[BD]_t$ are initial monomer concentration and the monomer concentration at time t , respectively, indicates a first order dependency of polymerization rate on monomer concentra-

tion: i.e. $R_p = k_p[C^*][BD]$, where R_p is a rate of polymerization, k_p is a rate constant of propagation, and $[C^*]$ is an active site concentration. The polymerization results are shown in Table 2. The stereoregularity of the polymers remains almost constant for the entire polymerization time, indicating identical nature of active centers. The MW of the polymers increases with conversion and the polydispersity is inclined to be increased at the longer polymerization time, most probably due to the crosslinking reactions activated at high conversion.

Along with the kinetic study, we have performed a series of reactions by varying parameters such as monomer concentration, cocatalyst amount, and reaction temperature, so as to investigate the effect of polymerization condition on catalytic activity and polymer microstructure. The **3a**/EASC catalyst system was chosen for the study and the results are summarized in Table 3. On increasing the initial monomer concentration from 0.3 to 1.0 M, the activity increases steadily with monomer concentration showing a first order dependency of polymerization rate on the initial monomer concentration and so does the MW of the polymer. This is in accordance with polymerization results from the kinetic study. The higher rate of polymerization can lead to higher MW, as the degree of polymerization is determined by the ratio of propagation and termination rates [36]. The stereoregularity of the polymers remains almost consistent within our experimental range. Even though no conspicuous variation of stereoregularity is marked according to $[Al]/[Co]$ ratio, both activity and MW change considerably according to $[Al]/[Co]$ ratio. The activity of the catalyst increases as the $[Al]/[Co]$ ratio increases from 50 to 400, and it decreases at high $[Al]/[Co]$ ratio (800), as usually observed in transition metal catalyzed olefin polymerizations combined with alkylaluminum cocatalysts. However,

Table 2
Effect of polymerization time on the of 1,3-butadiene (BD) polymerizations by 2,6-bis(benzimidazol-2-yl)-pyridine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst^a.

Entry	Time (min)	Yield (%)	M_n^b ($\times 10^{-5}$)	M_w/M_n^b	Microstructure (%) ^c		
					1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-
1	2	3.7	0.21	1.62	98.3	1.4	0.3
2	3	11.7	0.37	1.73	97.8	1.6	0.6
3	5	23.8	1.20	1.77	97.3	1.4	1.3
4	10	55.1	1.75	2.35	96.6	1.7	1.7
5	20	74.7	1.81	2.84	96.1	2.0	1.9
6	60	98.6	1.57	3.86	95.7	3.0	1.5

^a Polymerization conditions: catalyst = 2.5 μmol , $[Al]/[Co] = 400$, $[BD] = 0.7\text{ M}$, total reaction volume including toluene = 20 mL and temperature = 30 °C.

^b Measured by GPC.

^c Measured by ¹H and ¹³C NMR spectroscopies.

Table 3
Effect of various parameters on the polymerizations of 1,3-butadiene by 2,6-bis(benzimidazol-2-yl)-pyridine Co(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst^a.

Entry	$[Al]/[Co]$	$[BD]$	T (°C)	Yield (%)	M_n^b ($\times 10^{-5}$)	M_w/M_n^b	Microstructure ^c		
							1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-
1	400	0.3	30	37.1	0.44	1.73	97.7	1.7	0.4
2	400	0.4	30	43.3	1.14	1.60	97.2	1.6	1.2
3	400	0.5	30	48.3	1.34	1.87	97.6	1.4	1.0
4	400	0.7	30	55.1	1.75	2.35	96.6	1.7	1.7
5	400	1.0	30	58.7	2.59	2.36	96.1	2.1	1.8
6	50	0.7	30	8.1	0.88	1.40	96.9	1.8	0.3
7	100	0.7	30	38.1	1.36	2.15	96.1	1.6	0.4
8	200	0.7	30	49.7	1.54	2.61	96.4	2.2	1.4
9	800	0.7	30	43.7	1.59	2.46	95.9	2.7	1.3
10	400	0.7	0	–	–	–	–	–	–
11	400	0.7	50	80.1	0.79	3.01	94.1	5.7	0.2
12	400	0.7	70	75.5	0.50	5.21	87.3	12.2	0.9
13	400	0.7	90	47.4	0.33	3.80	78.6	20.4	1.4

^a Polymerization conditions: catalyst = 2.5 μmol , total reaction volume including toluene = 20 mL, and time = 10 min.

^b Measured by GPC.

^c Measured by ¹H and ¹³C NMR spectroscopies.

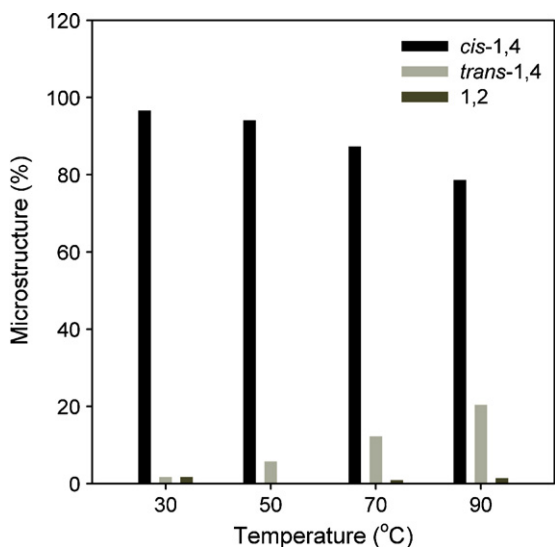


Fig. 5. Microstructure of polybutadienes produced by 2,6-bis(benzimidazol-2-yl)pyridine Co(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst at different temperatures. Polymerization conditions: catalyst = 2.5 μ mol, [Al]/[Co] = 400, [BD] = 0.7 M, total reaction volume including toluene = 20 mL, time = 10 min.

the trend of MW according to [Al]/[Co] ratio infers that chain transfer to aluminum is not significant for BD polymerization as in the case of olefin polymerizations.

The BD polymerization behavior by **3a**/EASC catalyst was highly sensitive to polymerization temperature. The catalyst system was inactive at 0 °C and the optimum activity is achieved at 50 °C with 80.1% conversion. Even though there was decrease in polymerization rate at higher temperature which is common in late transition metal catalyzed polymerization, the present catalytic system shows remarkable thermal stability yielding 75.5% conversion at 70 °C and even a conversion of about 50% at 90 °C. The MW of polymer decreases sequentially with an increase of temperature most probably due to facilitated chain transfer reactions at elevated temperature. But the most distinct feature of temperature study was in the variation of polymer microstructure with temperature. The extent of formation of *trans* isomer increased with polymerization temperature at the expense of *cis* isomer at high temperature, producing 20.4% *trans* isomer at 90 °C and thereby reducing *cis* content to 78.6% (Fig. 5). But the composition of 1,2-inserted isomer in the polymer did not show any marked deviation. The increased formation of *trans* content at elevated temperatures may be due to the facilitated *anti-syn* isomerization, as the energy requirement may be supplied by the higher polymerization temperature [35,36].

4. Conclusions

Taking advantage of the recent developments in ligand oriented approach in the field of coordination polymerization, we have designed, synthesized and characterized a series of cobalt(II) complexes of 2,6-bis(benzimidazolyl)pyridine ligands for the stereospecific polymerization of BD. The molecular structure elucidation by X-ray diffraction of complex **3c** shows that the metal center has a distorted square pyramidal geometry and the bis(benzimidazolyl) ligand can be viewed as essentially planar. The complexes when activated with alkylaluminum were highly active (>50% conversion within 10 min) to produce high MW polymers with predominantly *cis* configuration (up to 98%). Selection of cocatalysts remarkably influenced polymerization attributes. Among the cocatalysts employed, EASC was found to activate the catalyst most efficiently and the activity decrease in the order EASC > DEAC > MAO > MADC. When MAO and EASC were used as

cocatalyst, the stereospecificity was almost identical, but relatively higher percentage of *trans* insertion occurred while DEAC was used. The structural variation of catalyst through N-alkylation affects the activity most probably due to the electronic effect imposed on the active centers, while the stereospecificity remains almost unaffected. Kinetic study revealed a first order dependency of the polymerization rate on the initial monomer concentration. Of the various reaction parameters studied, temperature affected both the activity and more importantly the microstructure of the formed PBD. The extend of formation 1,4-*trans* inserted unit increased with increase in polymerization temperature possibly through a facilitated *anti-syn* isomerization. The catalytic system was also found to show considerable thermal stability, even yielding about 50% conversion at 90 °C.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.04.002.

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