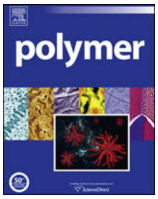
Polymer 50 (2009) 1150–1158

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Highly active and stereospecific polymerizations of 1,3-butadiene by using bis(benzimidazolyl)amine ligands derived Co(II) complexes in combination with ethylaluminum sesquichloride

Vinukrishnan Appukuttan, Lin Zhang, Chang-Sik Ha, Il Kim*

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

ARTICLE INFO

Article history:
Received 2 October 2008
Received in revised form
23 December 2008
Accepted 27 December 2008
Available online 10 January 2009

Keywords:
Polybutadiene
Stereospecific polymers
Transition metal chemistry

ABSTRACT

A family of cobalt(II) complexes supported on tridentate dibenzimidazolyl ligands having a general formula: $[N(CH_3)(CH_2)_2(Bm{-}R)_2]CoCl_2$ (where Bm = benzimidazolyl, R = H; –Me; –Bz), have been prepared by the condensation of *o*-phenylene diamine with methyliminodiacetic acid. The Co(II) complexes exhibited high activities for the polymerization of 1,3-butadiene, on activation with ethylaluminum sesquichloride (EASC), to yield predominantly *cis*-1,4 microstructure. The polymers are characterized by high molecular weight with polydispersity values between 2.35 and 3.37. The ligand modification shows remarkable influence on polymerization activity. The stereospecificity of the catalysts is consistent for a wide range of reaction conditions, except temperature. The electronic influence of ligand structure towards metal center is investigated by using cyclic voltammetric analysis and the generation of cationic active centers is identified *via* UV–vis spectroscopic analysis of the catalyst system.

1. Introduction

The elastomeric *cis*-1,4-polybutadiene (PBD) is one of the most important raw materials in rubber industry. 1,3-Butadiene (BD) polymerization may yield PBDs with different isomeric forms such as *cis*-1,4, *trans*-1,4, 1,2-syndiotactic, 1,2-isotactic, and 1,2-atactic and each shows different properties and consequently diverse applications [1,2]. Ziegler–Natta catalysts are highly chemo- and stereoselective in BD polymerization *via* coordination mode of polymerization compared to the radical and ionic counterparts [1]. The earlier explored stereospecific catalysts were based on AlR_3/TiX_n (X = halides, alcoholates) [2]. For the industrial production of PBD, catalysts based on carboxylates, acetylacetonates or alcoholates of Ti, V, Nd, Ni and Co are currently employed in combination with various organoaluminums [1–3].

The post-metallocene era has witnessed the emergence of various homogeneous catalysts of early to late transition metals for olefin polymerizations, bearing chelates with wide range of donor atoms [4]. An advantage of such ‘single-site’ catalysts in diene polymerization, apart from superior activity, is the achievement of superior control over the stereochemistry of resulting polymer by stereo-electronic modulation of the ligand environment around the metal center in a cost effective manner. Recently there are a number of reports derived from such organometallic complexes for BD polymerization which are proved to be highly stereospecific coupled with good activity [2,5]. Another emerging class of catalysts is lanthanocenes that produce PBD with exclusively *cis* to predominately *trans* forms depending on the structure of the lanthanides used [6,7].

Cobalt-based catalysts, due to their plausible potential as commercial catalysts, are the ones among the most investigated. The most important industrial catalysts are simple Co-carboxylates in combination with various organoaluminums yielding highly *cis*-1,4-PBDs. In addition, solubilized cobalt salts such as $CoX_2 \cdot 2PPh_3$, $CoX_2 \cdot PPh_3$/pyridine (X = Cl, Br) and $CoCl_2 \cdot (RO)_3PO$ are well exploited. Chelates of divalent cobalt such as bis(salicylaldehyde)Co were also demonstrated to be efficient for BD polymerization. Six kinds of chelates containing electron donor atom pairs consisting of (O,O), (O,N), (N,N), (O,S), (N,S), and (S,S) were found equally effective [8–12].

The due significance of the ligand environment towards the polymer microstructure and activity was established in our previous works with Co(II) catalysts based on pyridyl bis(imine) and salicylaldimine ligands [13,14]. The steric crowding around the Co(II) metal center induced by bulky substituents is an important factor for reducing yield and lowering molecular weight. Endo et al. found similar effect using Co/salen system [15]. As a continuation of this study to search for new Co(II) complexes effective for the

---

* Corresponding author. Tel.: +82 51 510 2399; fax: +82 51 512 8563.
E-mail address: ilkim@pusan.ac.kr (I. Kim).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.12.047

stereospecific polymerization of BD, we have investigated a very planar (N,N,N) type ligand systems of bis(benzimidazolyl)amines. Chromium(III) complexes bearing (N,N,N) type ligand were recently reported to produce highly *trans*-1,4-PBD in the presence of excess amount of methylaluminoxane (MAO) [16]. Herein, we are reporting a family of new Co(II) complexes bearing similar tridentate bis(benzimidazolyl) amine ligands for stereospecific BD polymerizations. These complexes are visualized to have a much open active center attached to planar ligand framework with no substantial adjacent bulky substituents. BD polymerizations have been performed employing various cocatalysts, with special emphasis on ethylaluminum sesquichloride (EASC), at various reaction parameters. The ligand electronic effect on the cobalt center is analyzed by cyclic voltammetric (CV) experiment and UV–vis spectroscopy study is performed to figure out mechanistic procedures of active sites formation.

2. Experimental section

2.1. General procedures and materials

All manipulations involving air or moisture sensitive compounds were carried out under a purified nitrogen atmosphere using Schlenk technique. Toluene was distilled over Na/benzophenone and stored over molecular sieves (4 Å). Tetrahydrofuran (THF) was dried over calcium hydride 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, 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.

UV–vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer in toluene at room temperature under nitrogen atmosphere. The CV measurements were conducted on a BAS CV-50 W voltammetric analyzer with scan rates of 100 mV/s. The electrolytic cell used was a conventional three-compartment cell, in which a glass carbon working electrode, a platinum counter electrode, and Ag/AgCl reference electrode were employed. The CV measurements of the complexes were performed under a nitrogen atmosphere at room temperature in dimethyl formamide (DMF) using 0.10 M tetrabutylammonium perchlorate (TBAP, TCI) as the supporting electrolyte. 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. Molecular weight (MW) and molecular weight distribution (MWD) of PBD were determined by gel permeation chromatography (GPC) using a Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at 25 °C on a Varian Gemini 2000 spectrometer in $CDCl_3$ containing tetramethylsilane as standard. All chemical shifts are reported in parts per million (ppm). The typical NMR chemical shifts for PBDs are as follows: ^{1}H NMR: $\delta = 4.8–5.2$ ($=CH_2$ of 1,2-BD unit), 5.2–5.8 (–CH of 1,4-BD unit and –CH of 1,2-BD unit). ^{13}C NMR: $\delta = 27.4$ (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).

2.2. Synthesis of ligands (Scheme 1)

The syntheses of ligands and Co(II) complexes are summarized in Scheme 1. The bis(benzimidazolyl)amine ligands, **1** and **2a** were prepared according to the reported procedures [17].

2.2.1. N-methyl-N,N-bis[(1-benzyl-1H-benzimidazol-2-yl)methyl]amine (**2b**)

To **1** (0.50 g, 1.72 mmol) in 15 mL of THF at 0 °C, sodium hydride (85%) (0.20 g, 6.87 mmol) was added. After 1 h of reaction, benzyl bromide (1.63 mL, 13.73 mmol) was added to the reaction mixture. The temperature was slowly raised to 50 °C and the reaction mixture was stirred over night. The mixtures were then added to the water, the off-white precipitate formed was filtered, washed extensively with water and one time with cold methanol. The compound was dried at 50 °C under vacuum. Yield: 75.4% (0.61 g). Mp: 180–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 2.43 (s, 3H), 3.84 (s, 4H), 5.06 (s, 4H), 6.74 (m, 4H), 7.19 (br m, 12H) 7.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.13, 142.30, 135.96, 135.58, 128.80, 127.65, 125.89, 123.03, 122.22, 119.90, 109.84, 54.15, 46.53, 43.63. Anal. Calcd. for $C_{31}H_{29}N_5$: C, 78.95; H, 6.20; N, 14.85. Found: C, 79. 08; H, 6.14; N, 14.78.

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

2.3.1. N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine cobalt (II) chloride (**3a**)

A mixture of **1** (0.60 g, 2.06 mmol) and $CoCl_2 \cdot 6H_2O$ (0.49 g, 2.06 mmol) was stirred in 10 mL of THF for 12 h at room temperature. The brilliant blue colored product precipitated was filtered, washed with THF (3 × 20 mL) and once with diethyl ether (20 mL), and then dried under vacuum. Yield 0.76 g (88%). Anal. Calcd. for $C_{17}H_{17}N_5$: C, 48.8; H, 4.07; N, 16.63. Found: C, 48.53; H, 4.09; N, 16.58. FAB-MS (*m*/*z*): 388 $[M–Cl]^+$, 807 $[2M–Cl]^+$, 769 $[2M–2Cl]^{2+}$.

2.3.2. N-methyl-N,N-bis[(1-methyl-1H-benzimidazol-2-yl)methyl]amine cobalt (II) chloride (**3b**)

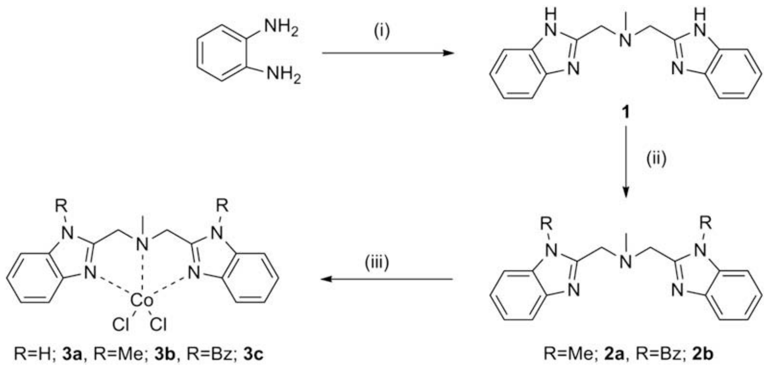
Similar procedures for **3a** were employed. Reaction of **2a** (0.50 g, 1.57 mmol) with $CoCl_2 \cdot 6H_2O$ (0.37 g, 1.57 mmol) yielded 0.64 g (91%) of blue solid. Anal. Calcd. for $C_{19}H_{21}N_5$: C, 50.8; H, 4.71; N, 15.87. Found: C, 50.86; H, 4.68; N, 15.86. FAB-MS (*m*/*z*): 415 $[M–Cl]^+$.

2.3.3. N-methyl-N,N-bis[(1-benzyl-1H-benzimidazol-2-yl)methyl]amine cobalt (II) chloride (**3c**)

Similar procedures for **3a** were employed. Reaction of **2b** (0.0.60 g, 1.27 mmol) with $CoCl_2 \cdot 6H_2O$ (0.30 g, 1.27 mmol) yielded 0.66 g (86%) of blue solid. Anal. Calcd. for $C_{31}H_{29}N_5$: C, 61.9; H, 4.86; N, 11.64. Found: C, 61.58; H, 4.86; N, 11.57. FAB-MS (*m*/*z*): 567 $[M–Cl]^+$.

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** (1.1 mg) was dissolved in 19.45 mL of toluene. After controlling 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, keeping overall yield less than about 70%. The resulting solution mixture was poured into acidified methanol (100 mL of a 5% v/v solution of HCl) containing butylhydroxytoluene as stabilizer. The polymer was isolated by filtration and washed with methanol, and then dried overnight at 50 °C under vacuum. Polymer yield was determined by gravimetry.



Scheme 1. Synthesis of complexes: (i) methyliminodiacetic acid, (ii) NaH/R–X (Me–I, Bz–Br), (iii) $CoCl_2 \cdot 6H_2O$.

3. Results and discussion

3.1. Synthesis and characterization of cobalt complexes

The bis(benzimidazolyl)amine ligand **1** was prepared by condensation reaction of 1,2-phenylenediamine and methyliminodiacetic acid in ethylene glycol at 190 °C. The ligands **2a** and **2b** were obtained in high yields through simple *N*-alkylation by corresponding alkyl halides *via* sodium salts of **1** in THF [17,18]. All of these ligands synthesized were confirmed by elemental analysis and NMR spectroscopy.

Cobalt complexes **3a**–**3c** were prepared in good yields *via* the treatment of corresponding ligands with 1 equiv of $CoCl_2 \cdot 6H_2O$ in THF at room temperature (Scheme 1). The blue colored cobalt complexes were consistent with their elemental analyses. The crystal structure of complex **3a**–methanol adduct was previously reported [18]. The cobalt center is described to have a distorted trigonal bipyramidal geometry with ligand coordinating facially. FAB-MS analysis of complex **3a** bearing no *N*-substituents revealed the existence of prominent molecular ion fragments at a high MW region, one at 807 and another at 769, apart from the expected m/z values at 388 formed by $[M–Cl]^+$ molecular ion (Fig. 1). This observation indicates most probably the formation of a dimeric complex through inter molecular hydrogen bonding between N–H groups of benzimidazolyl moiety. This could make the peaks at 807 possibly from a $[2M–Cl]^+$ molecular ion and at 769 from $[2M–2Cl]^{2+}$. Such dimeric complex is expected to be easily dissociated to monomeric species during the activation with organoaluminum cocatalysts. The cobalt complexes (**3b** and **3c**) bearing ligands with *N*-alkylated substituents showed no such dimerization process, as evidenced from the FAB-MS analysis data.

3.2. Effect of catalyst structure on solution polymerization of BD

The solution polymerizations of BD were carried out in toluene solvent. The polymerization results obtained by various cobalt complexes in combination with EASC are summarized in Table 1. All catalysts show a good stereospecific control of about 95% towards *cis*-1,4-PBDs. The catalysts showed significant influence on activity by virtue of their variation in the electronic environment endowed by *N*-alkyl substituents. The unsubstituted and benzyl substituted catalysts are found to be far more active than their methyl substituted analogue. The relatively high activity of **3a** might be attributed to the deprotonation during the activation with EASC, resulting in the formation of 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 [19]. Hence the formation of this anion makes the net electronic charge away from the active metal center, thereby increasing the activity. In the case of benzyl substituted complex (**3c**), when activated with EASC, ethyl anion (Et^-) generated from EASC molecule may abstract a proton from the secondary carbon

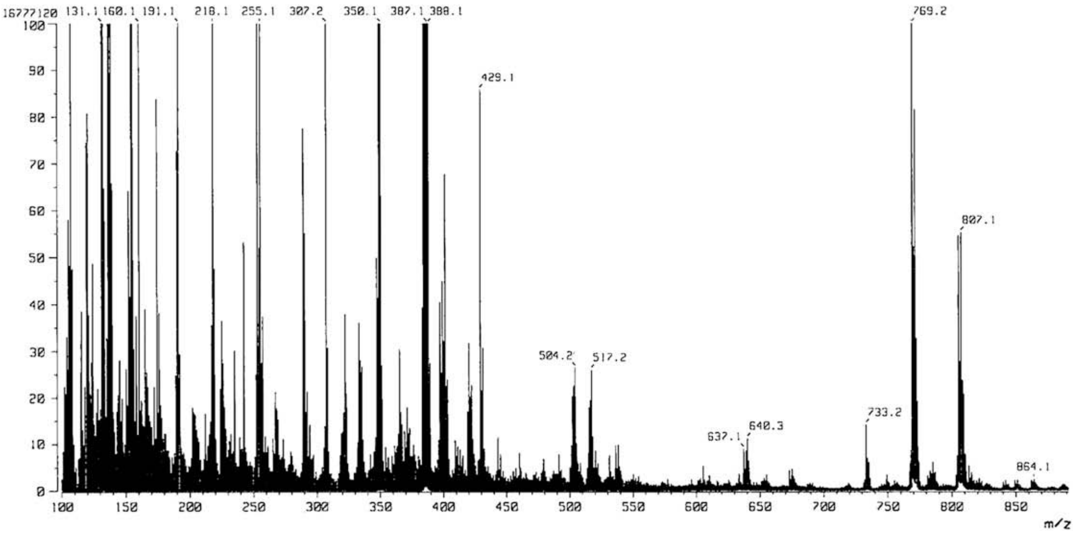


Fig. 1. The FAB-MS spectra of complex *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**).

Table 1
Polymerizations of 1,3-butadiene over various cobalt complexes of the general formula: $[N(CH_3)(CH_2)_2(Bm–R)_2]CoCl_2$, Bm = benzimidazolyl, **3a** (R = H); **3b** (R = $-CH_3$); **3c** (R = $-CH_2C_6H_5$) combined with various organoaluminum cocatalysts. Polymerization conditions: catalyst = 2.5 μmol, [Al]/[Co] = 400, [BD] = 0.7 M, total volume = 20 mL, time = 10 min, and temperature = 30 °C.

Entry	Catalyst	Cocatalyst[a]	Yield (%)	M_n[b] ($\times 10^{-5}$)	M_w/M_n[b]	Microstructure[c] (%)			X_n[d]	N[e] (mmol)
						1,4-*cis*	1,4-*trans*	1,2-inserted isomers		
1	**3a**	EASC	65.8	1.59	3.21	94.69	3.03	2.28	2940	0.31
2	**3b**	EASC	37.6	1.73	2.43	93.39	2.49	4.12	3198	0.17
3	**3c**	EASC	61.2	1.60	3.34	96.63	2.20	1.17	2958	0.29
4	**$CoCl_2$**	EASC	14.7	1.03	1.47	94.41	2.65	2.94	1904	0.11
5	**3a**	MAO	Trace	–	–	–	–	–	–	–
6	**3a**	MADC	Trace	–	–	–	–	–	–	–
7	**3a**	DEAC	26.2	0.20	2.03	79.41	11.79	8.80	370	0.99

[a] Organoaluminum cocatalysts: EASC = ethylaluminum sesquichloride; MAO = methylaluminoxane; MADC = methylaluminum dichloride; and DEAC = diethylaluminum chloride.

[b] Measured by GPC.

[c] Measured by ^1H and ^{13}C NMR spectroscopies.

[d] Degree of polymerization calculated from M_n and molecular weight of monomer.

[e] Number of polymer chains calculated from polymer yield and M_n.

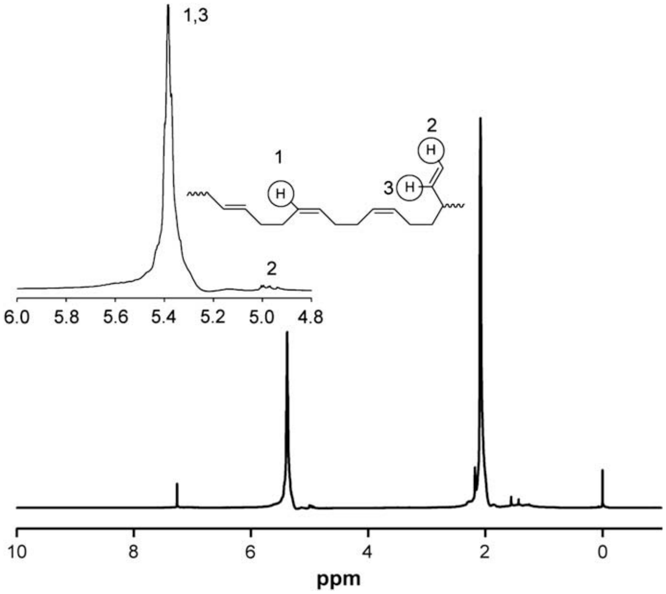


Fig. 2. ^1H NMR spectrum of the polybutadiene (Entry 1 in Table 1) synthesized by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride catalyst.

atom adjacent to an aromatic ring. This benzylic anionic species can be stabilized by a cationic Al species present in the system.

Puterbaugh and coworkers demonstrated the successful synthesis and stabilization of similar benzylic anions formed from benzyldimethylamine by sodium and lithium cations [20,21]. The formation of this anionic moiety makes a net flow of charge away from the metal center, making cobalt center more electropositive. In case of **3b**/EASC system, methyl substitution on *N*-atom of benzimidazolyl group with its electron donating inductive effect may direct the electrons towards the active metal center making it less electropositive, as indicated by its comparatively lower activity. Similar trend of activity increase with a net increase in electropositivity of metal center was observed in our previous report involving the polymerization of norbornene by Ni(II) diimine catalysts [22]. BD polymerization conducted with $CoCl_2$/EASC system under identical reaction conditions produced PBDs with a significantly lower conversion, elucidating the importance of ligand influence to the active center (Entry 4 in Table 1).

The stereoregularity of the resulting polymers was investigated by ^1H NMR and ^{13}C NMR spectroscopies. Figs. 2 and 3 show ^1H NMR and ^{13}C NMR spectra, respectively, of a representative PBD obtained by **3a**/EASC catalyst system (Entry 1 in Table 1). The microstructures were elucidated from the spectra in accordance with the reported literatures [9,23]. All the catalysts with different substitutions showed identical stereoselectivity (entries 1–3 in Table 1) with about 95% *cis*-1,4 stereoselectivity. This result demonstrates that the structure of the active centers of all catalysts is identical; however, it does not mean that their activities are similar since there is a big variation in activity according to the electronic environment. All the PBDs are characterized by high MW (M_n = 159,000–173,000) with MWDs ranging from 2.43 to 3.34. The PBD produced by $CoCl_2$ is consistent in its stereoregularity, but a relatively lower M_n and MWD is observed (entry 4 in Table 1).

3.3. Electrochemical analysis of cobalt(II) complexes

The backbone substitution of the ligand brings about significant perturbation in the electronic environment of the metal center of complexes. Electrochemical analysis of the resulting complexes can be a good tool to get insight on this effect. The successful applications of CV studies on ethylene polymerization catalysts were previously reported [24,25]. Cyclic voltammograms (Fig. 4) recorded for the complexes **3a**–**3c** in DMF display reduction waves between −1.00 and −1.70 V. Comparing the similar reduction wave observed in previous reports for Co(II) complexes based on terpyridine and pyridyl benzimidazol ligands, these reduction peaks are tentatively assigned to be originated from the reduction of metal center, Co(II) to Co(I) [26,27]. The reduction potential shows considerable variations for all the three complexes. Complexes **3a**–**3c** record a reduction potential of −1.05 V, −1.67 V, and −1.52 V,

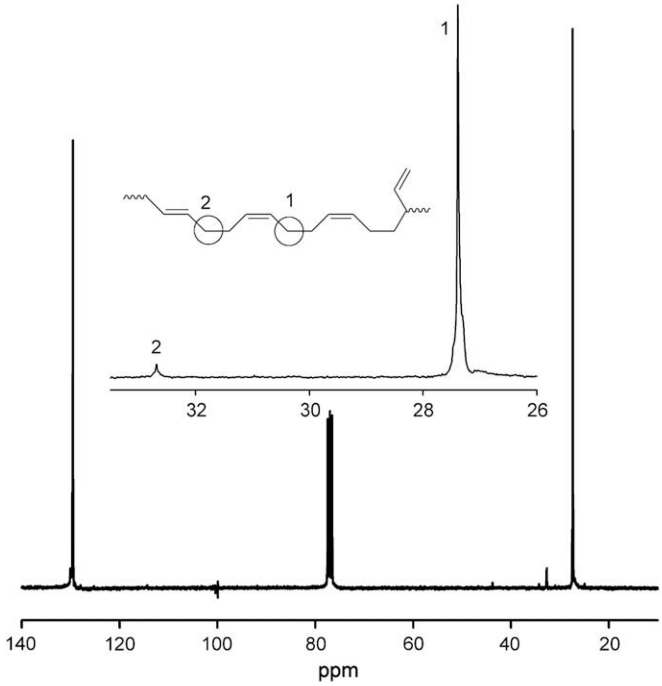


Fig. 3. ^{13}C NMR spectrum of the polybutadiene (Entry 1 in Table 1) synthesized by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride catalyst.

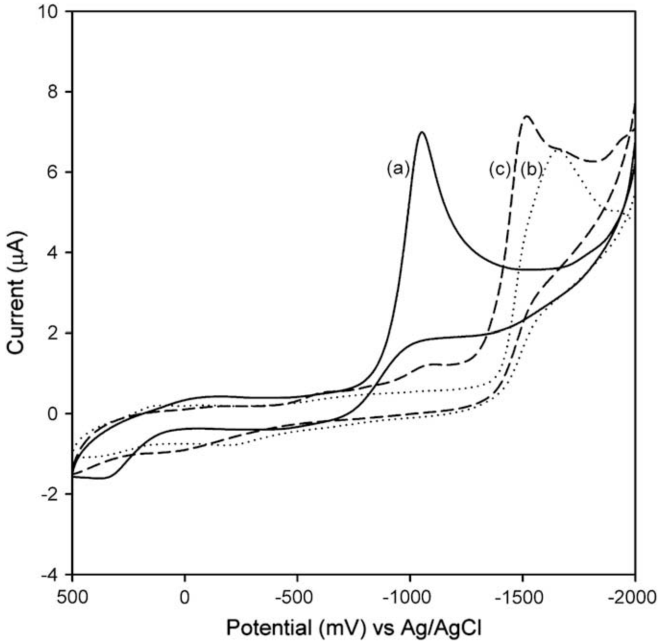


Fig. 4. Cyclic voltammograms of various cobalt complexes of general formula: $[N(CH_3)(CH_2)_2(Bm{-}R)_2]CoCl_2$, (Bm = benzimidazolyl); (a) R = H (**3a**), (b) R = $-CH_3$ (**3b**), and (c) R = $-CH_2C_6H_5$ (**3c**) in DMF at 25 °C. Scan rate is 100 mV/s.

respectively. Since the central metal portion ($CoCl_2$) is the same for all complexes, the change in the reduction potential is attributed to the variation in ligand structure brought about by the *N*-alkylation. The relatively easier reduction of the metal center in complex **3a** indicates that the metal is more electropositive than compound **3b**. Comparing the catalytic activity of **3a** with **3b** (entries 1 and 2, Table 1), the higher electropositivity of the metal center is more favorable to achieve higher activity. According to the reduction potential value obtained by **3c** complex, we may expect **3c** shows slightly higher activity than **3b**; however, the observed relatively high activity might be due to the formation of benzylic anion as discussed in the previous section along with electronic influence (entry 3, Table 1).

3.4. *Kinetics of BD polymerization*

A series of BD polymerizations initiated by **3a**/EASC ([Al]/[Co] = 400) were performed at 30 °C. The plot of polymer yield with polymerization time is depicted in Fig. 5. A sharp increase of the polymerization rate is observed during the early period (~10 min) of polymerization and then it increases monotonously till 60 min, attaining almost complete conversion of BD. The plots of $\ln[BD]_0/[BD]_t$ with polymerization time (Fig. 5), where $[BD]_0$ and $[BD]_t$ are initial monomer concentration and the monomer concentration at time *t*, respectively, show a good linear relationship indicating first order dependency of polymerization rate on monomer concentration: *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 M_n tended to increase with polymerization time up to 10 min and no significant changes were observed further. The MWD increased with time from 1.98 at 1 min to a broad one of 3.91 at 60 min. Results also showed the formation of polymers with almost similar stereoregularity throughout the entire polymerization time indicating identical nature of active center.

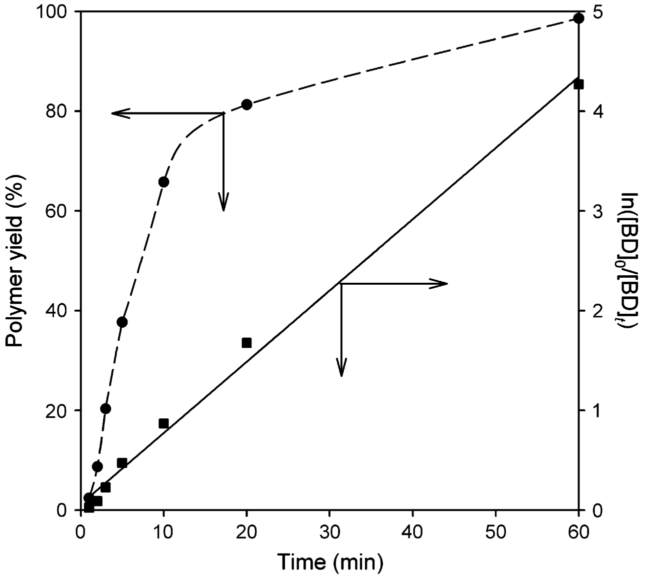


Fig. 5. The plots of polymer yield (●) and $\ln[BD]_0/[BD]_t$ (■) against polymerization time for BD polymerization by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride. Polymerization conditions: catalyst = 2.5 μmol, [Al]/[Co] = 400, [BD] = 0.7 M, total volume = 20 mL, temperature = 30 °C.

3.5. *Effect of polymerization parameters*

Since the stereoselectivity of catalysts is predominantly dependent upon the structural features of active center, the effects of type and amount of cocatalysts on active center are investigated. The **3a**/MAO and **3a**/MADC catalysts yield only negligible amounts of PBD (Table 1), while **3a**/DEAC catalyst (entry 7, Table 1) produces PBD with significantly low MW (M_n = 20,000) in 26.2% yield. It is interesting to note that the resulting PBD is characterized by comparatively higher content of *trans*-1,4 (11.78%) and 1,2-inserted isomers at the expense of *cis*-1,4 isomer. These results show that the nature of the active species is changed by forming different ion-pairs during polymerization resulting from the reaction between cobalt metal centers and different anionic cocatalysts. Comparing **3a**/DEAC with **3a**/EASC, it is expected that the relatively smaller size of DEAC molecule than that of EASC induces to form a tighter ion pair, thereby making the insertion of monomer much slower, resulting in relatively lower activity and MW, since the rate of termination may predominate over rate of propagation [28].

Apart from structural parameters of the complexes, the reaction conditions are another decisive factor in governing the

Table 2
Effect of polymerization time on the of 1,3-butadiene (BD) polymerizations by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst. Polymerization conditions: catalyst = 2.5 μmol, [Al]/[Co] = 400, [BD] = 0.7 M, total volume = 20 mL and temperature = 30 °C.

Entry	Time (min)	Yield (%)	M_n[a] ($\times10^{-5}$)	M_w/M_n[a]	Microstructure[b] (%)		
					1,4-*cis*	1,4-*trans*	1,2-inserted isomers
1	1	2.4	0.89	1.98	96.51	1.33	2.16
2	2	8.7	1.07	2.21	96.23	1.81	1.96
3	3	20.3	1.24	2.39	95.97	1.98	2.05
4	5	37.7	1.45	2.88	96.39	1.70	1.93
5	10	65.8	1.59	3.21	94.69	3.03	2.28
6	20	81.3	1.63	3.43	95.12	2.69	2.19
7	60	98.6	1.60	3.91	94.68	2.56	2.76

[a] Measured by GPC.
[b] Measured by ^1H and ^{13}C NMR spectroscopies.

Table 3
Effect of various parameters on the polymerizations of 1,3-butadiene (BD) by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride (EASC) catalyst. Polymerization conditions: catalyst = 2.5 μmol, total volume = 20 mL, and time = 10 min.

Entry	[Al/Co]	[BD]	Temp. (°C)	Yield (%)	M_n[a] ($\times 10^{-5}$)	M_w/M_n[a]	Microstructure[b]		
							1,4-*cis*	1,4-*trans*	1,2-inserted isomers
1	400	0.3	30	36.9	0.65	2.19	95.20	2.80	1.00
2	400	0.4	30	53.1	0.97	2.25	95.77	2.45	1.78
3	400	0.5	30	64.5	1.35	3.17	95.75	2.75	1.50
4	400	0.7	30	65.8	1.59	3.21	94.69	3.03	2.28
5	50	0.7	30	14.1	0.88	2.66	97.75	1.23	1.02
6	100	0.7	30	17.3	1.02	2.41	96.35	1.38	2.27
7	200	0.7	30	45.9	1.47	2.61	96.89	2.06	1.05
8	800	0.7	30	66.5	1.69	3.11	96.07	2.60	1.33
9	1600	0.7	30	51.5	0.94	2.99	96.50	1.88	1.62
10	400	0.7	50	58.8	1.24	3.26	91.57	6.06	2.37
11	400	0.7	70	57.0	1.07	2.77	77.04	14.00	8.96
12	400	0.7	90	27.3	0.34	2.35	74.12	15.80	10.08

[a] Measured by GPC.
[b] Measured by ^1H and ^{13}C NMR spectroscopies.

stereochemistry and activity of catalysts. The results obtained by changing the polymerization parameters such as monomer concentration, [Co]/[Al] ratio and reaction temperature are summarized in Table 3. The activity and the MW of the resulting PBD are proportional to [BD] in the range from 0.3 M to 0.7 M. This indicates a first order monomer dependency on the propagation rate, akin to the observations from kinetic study. Since the average degree of polymerization is directly proportional to overall rate of propagation and conversely to the transfer reactions, a higher conversion might lead to a higher molecular weight [28]. The variation of monomer concentration showed no significant effect on the microstructure of resulting polymers.

In order to investigate the effect of cocatalyst concentration, a series of polymerizations were performed with increasing [Al]/[Co] ratios from 50 to 1600 by using **3a**/EASC system (entries 4–9, Table 3). Yield increases sharply from 14% to 65.8% as [Al]/[Co] ratio increases from 50 to 400, levels off in the range from 400 to 800, and then declines to lower yield at [Al]/[Co] = 1600. Generally, in olefin polymerizations, an increase in the cocatalyst concentration decreases the MW of the polymer due to the facilitated chain transfer reactions to aluminum [28]. In the present condition, it was observed that there is a prominent increase in molecular weight with increase in [Al]/[Co], demonstrating that the chain transfer to aluminum is not a significant reaction in BD polymerization (entries 4–8 in Table 3). The stereoselectivity is not so deeply influenced by the variation of the cocatalyst concentration.

The BD polymerizations were also carried out at a temperature ranging from 0 to 90 °C (entries 4, 10–12, Table 3). The polymerization at 0 °C gives no activity. The highest activity is observed at 30 °C and then decreased monotonously up to 70 °C. The activity decrease is more evident at 90 °C. This decreasing trend of activity at higher temperature might be due to the deactivation of active species at higher temperatures [4]. Also there is a decrease in MW with temperature due to the enhanced rate of chain transfer processes. One of the most distinguishing features of the effect of temperature is its direct influence on PBD microstructure. Polymerizations at higher temperatures result in the formation of polymers with fairly high contents of *trans*-1,4 and 1,2-inserted PBDs (Fig. 6). As a result, PBD polymerized at 90 °C consists of 15.80% of *trans*-1,4, 74.12% of *cis*-1,4, and 10.08% of 1,2-inserted isomers, which is comparable to PBD obtained at 30 °C consisting of 3.03% of *trans*-1,4, 94.69% of *cis*-1,4, and 2.28% of 1,2-inserted isomers.

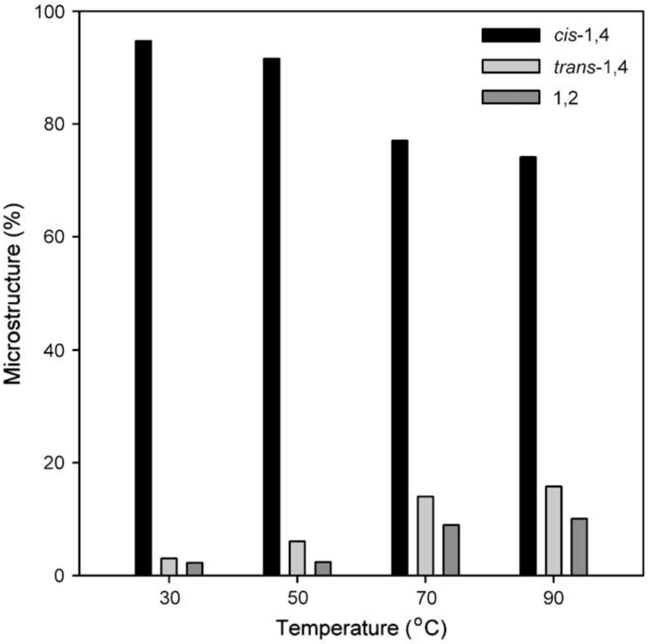
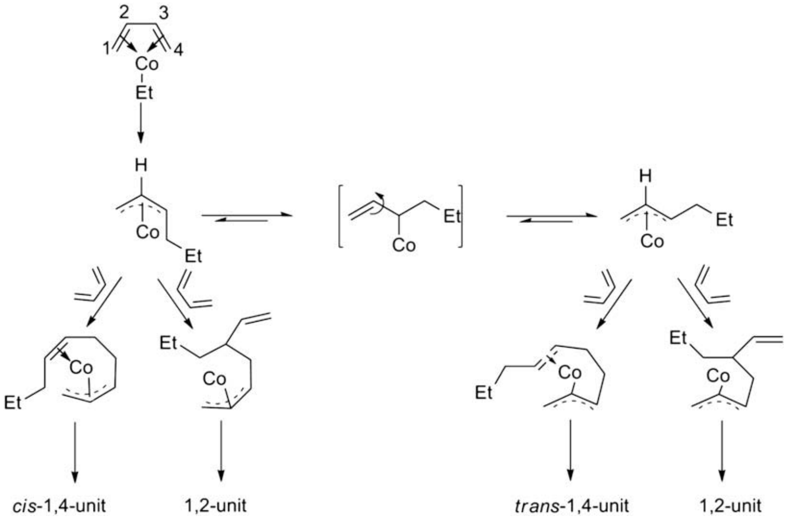


Fig. 6. Microstructure of polybutadienes produced by *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**)/ethylaluminum sesquichloride at different temperatures. Polymerization conditions: catalyst = 2.5 μmol, [Al]/[Co] = 400, [BD] = 0.7 M, total volume = 20 mL, time = 10 min.

3.6. Mechanistic considerations

The presence of conjugated double bond in BD makes the polymerization mechanism complicated, resulting in PBDs with diverse microstructures. In fact, all the proposed mechanisms for the coordination polymerization involving conjugated dienes are identical irrespective of the active metal center [1,29]. As in the case of α-olefins the primary steps in diene polymerization involves the coordination of incoming monomer to the active site followed by its insertion into metal carbon bond. An essential difference for BD polymerization is that the mode of interaction of growing polymer chain with metal center is π-allylic type, involving a pseudo secondary insertion of the monomer, rather than a σ type for monoalkenes [1,30]. Moreover, the coordination of monomer to the metal center could adopt different conformations and hapticities. The favored way of approaches is *cis*-η^4 and *trans*-η^4, both involving the two double bonds of BD or by a *trans*-η^2 mode through only one of the double bonds [1]. Scheme 2 represents the possible mechanistic pathway of BD polymerization by Co(II) complexes of the present study, for clarity the ligand coordinated to metal center is eliminated from the scheme [1,29]. Energetically a *cis*-η^4 mode coordination of incoming BD to active cobalt center is preferred over the other two manners. Moreover, the spatial arrangement of cobalt favors an orbital overlap leading to a *cis*-η^4 mode of coordination with BD [31]. This BD monomer, coordinated to cobalt center in a *cis*-η^4 mode, inserts into the growing chain forming η^3-allyl coordinated terminal group which takes preferably an *anti* conformation. The coordination–insertion mechanism happening *via trans*-η^4 or *trans*-η^2 will result in a *syn* η^3-allyl coordinated terminal group. For terminal butenyl group devoid of any C2 substitution (as in the case of BD), *syn* conformation is believed to be thermodynamically more stable. Thus a *syn* form could also be resulted from an *anti*–*syn* isomerization [1,29].

The formation of an allylic end group makes C1 and C3 (Scheme 2) positions reactive for the next insertion which determines the chemoselectivity of the polymerization process, *i.e.* the formation



Scheme 2. Proposed mechanism for stereochemical control in 1,3-butadiene polymerization by cobalt(II) complex.

of 1,2-units relative to 1,4-units. The insertion at C1 will result in 1,4-units and that at C3 in 1,2-form. It is believed that, from the polymerization results obtained by **3a**/EASC system, C1 is attacked preferentially over C3 forming a 1,4 growing chain. The formation of *anti* or *syn* form is a decisive factor in determining spatial orientation of the growing polymer chain. The *anti*-conformer results in *cis*-1,4-PBDs while the *syn*-conformer gives *trans*-1,4-PBDs. It could be assumed that an *anti*-conformer is preferred in the present system considering the kinetic reasons, since primary coordination proceeds through a more stable *cis*-η^4 manner [1].

Taube et al. reported the existence of back biting interaction, η^2 type, through the double bond of penultimately inserted monomer in the growing chain along with the η^3-allyl coordination of last inserted one [32–34]. It was also inferred that the presence of ancillary ligands favored *anti*–*syn* isomerization resulting in more *trans* product [34]. Recently Costabile et al., showed experimentally the backbiting coordination of the double bond of the penultimate monomer in the polymer chain which in turn stabilizes *anti*-allyl group. This makes *anti*–*syn* isomerization which involves the rearrangement of conformation of last inserted unit an energetically demanding process, but not a forbidden one [35].

The present BD polymerization system, devoid of any bulky ancillary ligand, had a significant temperature effect on the microstructure of the polymers as illustrated by Fig. 5. Higher polymerization temperature enhanced the relative formation of *trans*-1,4 and 1,2-inserted isomers at the expense of *cis*-1,4 isomer. The energy requirement for a possible *anti*–*syn* isomerization may be supplied by the higher polymerization temperatures as verified by the increment in *trans* product with temperature. Another remarkable observation was the considerable reduction in the *cis* isomer to *trans* isomer on changing the cocatalyst from EASC to DEAC (entry 6, Table 1). As explained earlier the tight ion pair formation owing to the smaller size of DEAC might make the propagation step slower. This slower propagation rate can be a factor to promote the formation of thermodynamic product, the *trans* isomer, through an *anti*–*syn* isomerization [1].

3.7. UV–vis spectroscopic analysis

Processes involving the active species generation have been successfully evaluated by UV–vis spectroscopy for metallocene catalyst system by Cramail and coworkers [36–39]. They further extended their study to Ni-diimine catalysts [40]. In our previous study with Co(II) salicylaldimine catalysts, we have employed similar spectroscopic analysis to reveal successive elementary steps generating cationic active species for BD and ethylene polymerizations [14,41]. UV–vis spectra were recorded for all complexes under conditions similar to polymerization environments (Fig. 7). All the complexes show a characteristic absorption maximum centered at 618 nm, with no other peaks from 400 to 900 nm. Addition of 50 equiv of BD imparts no change to the spectra (for clarity this is not shown in Fig. 7). On adding EASC ([Al]/[Co] = 400) to the complex/BD mixture, two peaks are generated, one having strong absorption maxima at 497 nm and the other having weak but broad one between 800 and 900 nm with the disappearance of the peak at 618 nm.

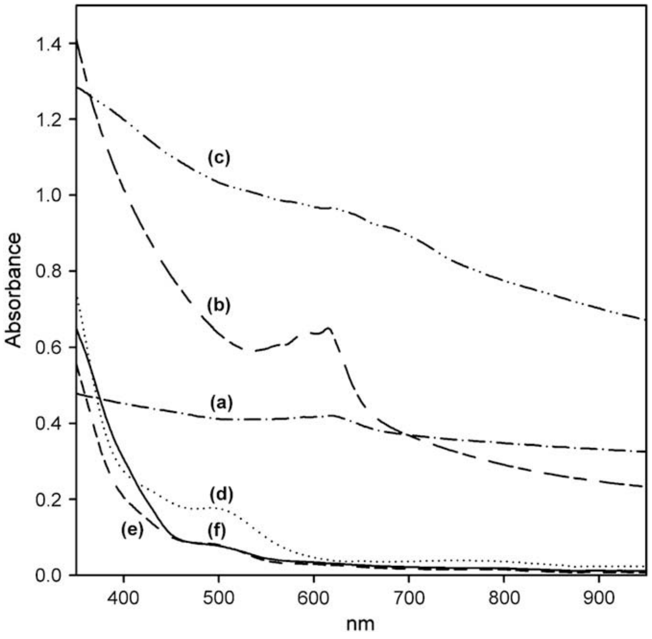


Fig. 7. UV–vis spectra of complexes $[N(CH_3)(CH_2)_2(Bm{-}R)_2]CoCl_2$ (Bm = benzimidazolyl, **3a**, R = H; **3b**, R = $-CH_3$; **3c**, R = $-CH_2C_6H_5$), 1,3-butadiene and ethylaluminum sesquichloride mixture in toluene solution: (a) **3a**, (b) **3b**, (c) **3c**, (d) **3a**/BD/EASC (1/50/200), (e) **3b**/BD/EASC (1/50/200), (f) **3c**/BD/EASC (1/50/200).

To follow the formation of active species we performed another set of UV–vis analysis with sequential addition of EASC in small increments ([Al]/[Co] = 50–800) to a mixture of **3a**/BD (Fig. 8). The addition of 25 equiv of EASC generates peaks at 497 nm and at 800–900 with a decrease in the intensity of the peak of the complex **3a** at 618 nm (Curve c, Fig. 8). As the amount of EASC increases, the intensity of the peak at 497 nm increases considerably, attaining a maximum at [Al]/[Co] = 800. The absorption peak at 618 nm observed for pure **3a** decreases gradually with increasing EASC and finally disappeared at higher cocatalyst ratio, demonstrating complete activation. From the careful examination of the UV–vis analysis and the polymerization results (Entries 4–8 in Table 3) at different cocatalyst concentrations, it can be concluded that there is a sequential increase in activity with increase in [Al]/[Co] ratio, reaching a maximum yield at 800 equiv. These observations substantiate the data collected from the UV–vis study that the peak at 497 nm is most probably generated by the addition of EASC due to the formation of the cationic active centers.

The spectra of [**3a**]/[BD]/[EASC] (1/50/25) mixture show absorption peaks indicating the existence of both active species (497 nm) and unreacted **3a** (618 nm), evidenced by low polymerization yield. Slower initiation process may result in a broad MWD of polymers as previously reported for BD polymerization using Co/salen complexes [18]. The slower rate of initiation might result in the variation of active species concentration with time and hence resulting in a broader MWD especially for a shorter reaction time of 10 min. In order to check the thermal stability of the active species, the UV–vis spectra of [**3a**]/[BD]/[EASC] mixtures were also recorded after ageing (keeping the mixture for 1 h at 90 °C). The peak at 497 nm is completely disappeared (Curve h, Fig. 8) and the addition of BD to this solution gives no polymer due to the deactivation of the active species. In addition the result collected from ageing test demonstrates again that the peak at 497 nm is originated from the formation of active species.

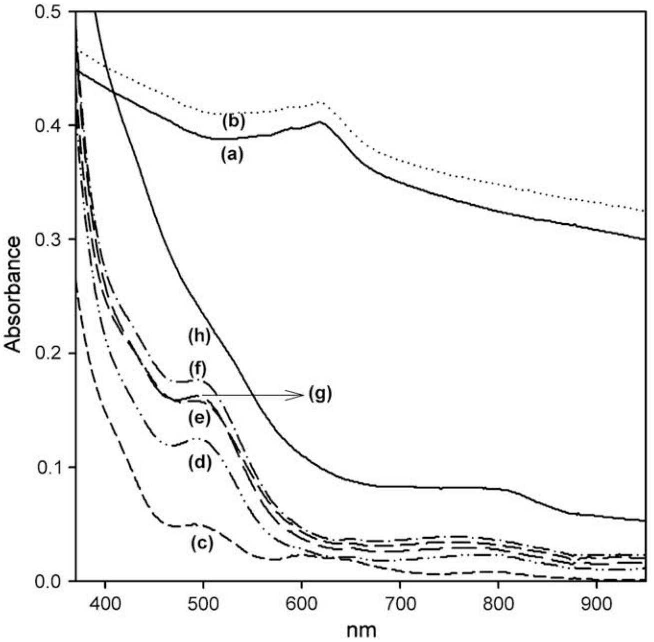


Fig. 8. UV–vis spectra of complex *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine cobalt(II) chloride (**3a**), 1,3-butadiene and ethylaluminum sesquichloride mixture in toluene solution: (a) **3a** alone, (b) **3a**/BD (1/50, molar ratio), (c) **3a**/BD/EASC (1/50/25), (d) **3a**/BD/EASC (1/50/50), (e) **3a**/BD/EASC (1/50/100), (f) **3a**/BD/EASC (1/50/200), (g) **3a**/BD/EASC (1/50/400), and (h) **3a**//EASC (1/400) mixtures after ageing for 1 h at 90 °C.

4. Conclusions

As a means of developing a new highly active and stereospecific catalyst systems for BD polymerization, we have synthesized a family of cobalt(II) complexes with a planar ligand framework based on bis(benzimidazolyl)amine with no substantial adjacent substituents and as a result with quite opened active centers. These complexes were found to produce PBDs with *cis* isomer content up to 97% in the presence of EASC as a cocatalyst. Electronic modulations of the complexes through *N*-alkylation of the ligands had a significant effect on the catalytic activity but not on the stereospecificity. The electronic effect was deduced by using cyclic voltammetric measurements. Variation on both BD monomer and cocatalyst concentrations altered the catalytic activity and the MW of PBD without seriously affecting the stereoregularity of the polymers. The polymerization temperature was an important parameter in changing the stereoregularity of the resulting PBDs. The extent of *trans*-1,4 isomer increased at the expense of *cis*-1,4 isomer content with increasing temperature, most plausibly due to a facilitated *anti–syn* isomerization at elevated temperatures. Changing the cocatalyst from EASC to DEAC also affected the polymer microstructure with considerable loss in activity and MW. The formation of cationic active sites was identified *via* detailed UV–vis spectroscopic analysis under similar conditions with polymerization.

Acknowledgement

This work was financially supported by the *World Class University Program* (No. R32-2008-000-10174-0). The authors are also grateful to the BK 21Project, and the National Core Research Center Program from MOST and KOSEF (R15-2006-022-01002-0).

References

[1] Thiele SK-H, Wilson DR. J Macromol Sci Part C Polym Rev 2003;43:581–628.
[2] Proto A, Capacchione C. In: Baugh LS, Canich JAM, editors. Stereoselective polymerization with single-site catalysts. New York: Taylor and Francis; 2008. p. 447–73.
[3] Cao L, Dong W, Jiang L, Zhang X. Polymer 2007;48:2475–80.
[4] Ittel SD, Johnson LK, Brookhart M. Chem Rev 2000;100:1169–204.
[5] Kaminsky W, Hinrichs B, Rehder D. Polymer 2002;43:7225–9.
[6] Kaita S, Takeguchi Y, Hou Z, Nishiura M, Doi Y, Wakatsuki Y. Macromolecules 2003;36:7923–6.
[7] Kaita S, Yamanaka M, Horiuchi AC, Wakatsuki Y. Macromolecules 2006;39:1359–63.
[8] Takeuchi M, Shiono T, Soga K. Polym Int 1995;36:41–5.
[9] Nath DCD, Shiono T, Ikeda T. Macromol Chem Phys 2002;203:756–60.
[10] Nath DCD, Shiono T, Ikeda T. Appl Catal A General 2003;238:193–9.
[11] Brady M, Cann KJ. U.S. Patent 5,879,805; 1999.
[12] Castner KF. U.S. Patent 5,448,002; 1995.
[13] Ung KB, Kim JS, Lee KJ, Ha CS, Kim I. Stud Surf Sci Catal 2006;159:873–6.
[14] Chandran D, Kwak CH, Ha CS, Kim I. Catal Today 2008;131:505–12.
[15] Endo K, Kitagawa T, Nakatani K. J Polym Sci Part A Polym Chem 2006;44:4088–94.
[16] Jacobsen GB, Chirinos-Colina JJ, Gibson VC. WO 2007/015074 A1; 2007.
[17] Gibson VC, Tomov A. WO 2004/083263 A1; 2004.
[18] Kwaskowska-Chec E, Kubiak M, Glowiak T, Ziolkowski JJ. J Chem Crystallogr 1995;25:837–40.
[19] Zhang W, Sun WH, Zhang S, Hou J, Wedeking K, Schultz S, et al. Organometallics 2006;25:1961–9.
[20] Puterbaugh WH, Hauser CR. J Am Chem Soc 1963;85:2467–70.
[21] Puterbaugh WH, Hauser CR. J Org Chem 1963;28:3465–7.
[22] Appukuttan V, Kim JH, Ha CS, Kim I. Korean J Chem Eng 2008;25:423–5.
[23] Clague ADH, Broekhoven JAM, Blaauw LP. Macromolecules 1974;7:348–54.
[24] Gibson VC, Long NJ, Oxford PJ, White AJP, Williams DJ. Organometallics 2006;25:1932–9.
[25] Bahuleyan BK, Son GW, Park DW, Ha CS, Kim I. J Polym Sci Part A Polym Chem 2008;46:1066–82.
[26] Marquez VE, Anacona JR, Barbarin CR. Polyhedron 2001;20:1885–90.
[27] Zhong C, He A, Wu GQ, Huang H. Synth Met 2008;158:33–7.
[28] Resconi L, Camurati I, Sudmeijer O. Top Catal 1999;7:145–63.
[29] Porri L, Giarrusso A, Ricci G. Prog Polym Sci 1991;16:405–41.
[30] Costabile C, Pragliola S, Pelosi L, Longo P. Polymer 2007;48:3059–65.

[31] Boor JJ. Ziegler–Natta catalysts and polymerizations. New York: Academic Press; 1979 [chapter 14].
[32] Tobisch S, Bögel H, Taube R. Organometallics 1996;15:3563–71.
[33] Tobisch S, Bögel H, Taube R. Organometallics 1998;17:1177–96.
[34] Taube R, Schmidt U, Gehrke JP, Anacker U. J Prakt Chem 1984;326:1–11.
[35] Costabile C, Pragliola S, Longo P. J Polym Sci Part A Polym Chem 2006;44:1343–6.
[36] Coevet D, Cramail H, Deffieux A. Macromol Chem Phys 1998;199:1451–7.
[37] Coevet D, Cramail H, Deffieux A. Macromol Chem Phys 1998;199:1459–64.
[38] Coevet D, Cramail H, Deffieux A, Maldenov C, Pedeutour JN, Peruch F. Polym Int 1999;48:257–63.
[39] Pedeutour JN, Radhakrishnan K, Cramail H, Deffieux A. Polym Int 2002;51:973–7.
[40] Peruch F, Cramail H, Deffieux A. Macromolecules 1999;32:7977–83.
[41] Chandran D, Kwak CH, Oh JH, Ahn IY, Ha CS, Kim I. Catal Lett 2008;125:27–34.