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Polymerization of 1,3-butadiene by bis(salicylaldiminate)cobalt(II) catalysts combined with organoaluminium cocatalysts

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Abstract

The one-pot reactions of salicylaldehyde or its derivatives with 2,6-dialkyl substituted anilines in the presence of metallating agent, $Co(OAc)_2.4H_2O$, yield a series of cobalt(II) complex precatalysts (Ar^1-N=C-Ar^2-O$)_2$Co (**1**, Ar^1 = 2,6-dimethylaryl, Ar^2 = aryl; **2**, Ar^1 = 2,6-diethylaryl, Ar^2 = aryl; **3**, Ar^1 = 2,6-diisopropylaryl, Ar^2 = aryl; **4**, Ar^1 = 2,6-dimethylaryl, Ar^2 = 3-*t*-butylaryl; **5**, Ar^1 = 2,6-diethylaryl, Ar^2 = 3-*t*-butylaryl; **6**, Ar^1 = 2,6-diisopropylaryl, Ar^2 = 3-*t*-butylaryl) in high yields. The treatment of these cobalt(II) salicylaldimine complexes with ethylaluminum sesquichloride (EAS) forms highly active 1,3-butadiene (BD) polymerization catalysts, yielding polybutadienes of moderate molecular weights (MW = 33,900–44,500) with narrow molecular weight distributions (MWD = 1.29–2.36). All Co(II) complexes yield highly *cis*-1,4-polybutadienes (>94%) with negligible amounts of 1,4-*trans* (<2.32%) and 1,2-added (<3.37%) products in polymerizations at 30 °C combined with EAS. As the steric bulk at the cobalt center increases by changing the alkyl substituents on the ligand environment, 1,4-*cis* content decreases. The *cis* content and MW decrease as polymerization temperature increases. The polymerization yield and the *cis* content increase as BD concentration increases. The nonlinearity of [BD] to yield and [BD] to MW relationships demonstrates that the narrow MWD comes from uniform active species present in the polymerization system. The activation procedures of the Co(II) complexes in conjunction with EAS are studied by using UV-visible spectroscopy. Suitable correlations are found between polymerization activities and the changes in UV-visible absorption spectra of the complex.

Keywords: 1,3-Butadiene; Catalysis; Cobalt salicylaldimine complexes; Polymerization; Stereoregular; Transition metal chemistry

1. Introduction

High *cis*-1,4-polybutadiene (PBD) is produced commercially by the solution polymerization of 1,3-butadiene (BD) via Ziegler–Natta catalysis. The polymerization of conjugated diolefins is more complicatedly diverse and perplexing than the polymerization of α-olefins [1]. Since the scientific boom produced by the emergence of metallocene catalysts for ethylene polymerization, significant efforts have been directed toward the discovery and application of new, highly active, single-site catalysts. Such efforts introduced quite a large number of postmetallocene catalysts based on both early and late transition metals. There are a number of such organometallic complexes having late transition metals used in olefin polymerization reactions. However, there have been a few reports on successful extension of such catalysts for butadiene polymerization. This may be due to the understanding of these systems are still incomplete. In BD polymerization, major number of catalysts is based on carboxylates, acetylacetonates, or alcoholates of Ti, Nd, Ni and Co [1]. Organometallic catalysts with well-designed structure are few in number.

Cobalt-based catalysts have been widely investigated, probably because they have their attractiveness as potential commercial catalysts [2–7]. Unexpectedly high activity of Co systems among the non-d^0 families in BD polymerization also attracts much academic interest. The most important catalysts contained solubilized cobalt salts plus $AlEt_2Cl$ such as $CoCl_2 \cdot 2$ pyridine and $CoCl_2 \cdot (RO)_3PO$. Chelates of divalent cobalt were also effective, such as bis(salicylaldehyde)Co: six kinds of chelates containing electron donor atom pairs such as (O,O), (ON), (N,N), (O,S), (N,S), and (S,S) were found equally effective [2–7].

As a continuation of the study searching a new suitable chelate of divalent cobalt effective for the stereospecific

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polymerization of BD, we chose salicylaldimine ligands, which have been well known for the synthesis of bis(phenoxy-imine) titanium complexes (known as FI catalyst), yielding highly active olefin polymerization catalysts in conjunction with methylalumoxane [8]. Here, we are reporting a series of catalyst systems based on cobalt salicylaldimine/ethylaluminium sesquichloride (EAS) and our attempts to study the factors influencing the microstructure of BD polymer. The formation procedures of active sites from the reaction of cobalt complex with EAS, followed by the addition of BD were studied by UV-visible spectroscopy.

2. Experimental

2.1. General procedure

All reactions and operations were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. Polymerization grade BD (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX^{TM} catalyst and molecular sieve 5 Å/13X. Ethanol used for the precatalyst synthesis was dried over calcium hydride and stored over molecular sieves (4 Å). Toluene used as solvent for polymerizations was distilled from Na/benzophenone and stored over molecular sieves (4 Å). EAS (25 wt% solution in toluene) and all other reagents were purchased from Aldrich Chemical Co. and used without further purification.

2.2. Characterizations

UV–vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer in toluene. IR spectra were recorded on Shimadzu Fourier Transform Infrared spectrometer IRPrestige-21 by making KBr pellets of the samples. Elemental analysis of metal complexes was carried out using Vario EL analyzer. Molecular weight (MW) and molecular weight distribution (MWD) of PBD were determined by gel permeation chromatography (GPC) using a Waters M515 series system in tetrahhydrofuran (THF) at 25 °C as calibrated with polystyrene standards. The microstructure of PBD was determined by using ^{1}H-NMR and ^{13}C-NMR spectra recorded on a Varian Gemini 2000 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer in $CDCl_3$ at 25 °C. All chemical shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ (δ 7.24) for ^{1}H NMR and $CDCl_3$ (δ 77.00) for ^{13}C NMR. ^{1}H NMR: δ = 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: 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).

2.3. Preparation of complexes

The bis(salicylaldiminate)cobalt(II) complexes were synthesized based on the reported procedure [9,10] of its nickel counterparts. In a typical procedure, salicylaldehyde (0.13 mL, 1.17 mmol) or 3-*tert*-butyl-salicylaldehyde (0.2 mL, 1.17 mmol) was allowed to react with an equimolar amount of $Co(OAc)_2.4H_2O$ (0.274 g, 1.17 mmol) and 3 equiv. of the proper amine (3.5 mmol) in 100 mL of ethanol at the refluxing temperature for 4 h. After cooling to room temperature, the resulting mixture was precipitated in *n*-hexane. The filtered solid was washed and then dried in vacuo at 50 °C.

Complexes **1**, **2**, **3**, **4**, **5**, and **6** were obtained as off white colored crystals. Characteristics of the complexes are summarized in Table 1.

2.4. Polymerization procedure

Solution polymerizations of BD were carried out in a glass reactor (40 mL) connected with a vacuum system. A 2.8 μmol of the precatalyst (1.4 mg (**1**), 1.6 mg (**2**), 1.7 mg (**3**), 1.7 mg (**4**), 1.9 mg (**5**), 2.1 mg (**6**)) was dissolved in 20 mL of toluene. After controlling the temperature of reaction mixture (10 to 70 °C), suitable amounts of BD (0.2–2.0 M) were equilibrated to toluene. The polymerization started by injecting prescribed amounts of EAS (100–400 equiv.) to the solution. The polymerization time was controlled to 10 min for facile agitation. The resulting solution was poured into acidified methanol (100 mL of a 5% *v*/*v* solution of HCl). The polymer was isolated by filtration and washed with methanol, then dried overnight at 40 °C. Polymer yield was determined by gravimetry.

We have carried out a number of experiments and the value presented in Tables 2–4 are those given at least two concordant values. Considering all the experiments done in this regard, the reproducibility of the number average molecular weights were having a percentage error of ±0.8, and we could make out similar observations on other parameters such as yield,

Table 1
Characterizations of cobalt(II) salicylaldimine complexes

Compd.	Molecular formula[a]	Yield (%)	Element analysis C/H/N		IR analysis (cm^{-1})		UV–vis (nm)[b]
			Cald	Found	ν(C=N)	ν(C–O)	
1	$Co(C_{15}H_{14}NO)_2$	68	71.00/5.56/5.52	71.15/5.60/5.48	1564	1419	487
2	$Co(C_{17}H_{18}NO)_2$	65	72.46/6.44/4.97	72.51/6.46/4.94	1563	1422	487
3	$Co(C_{19}H_{22}NO)_2$	65	73.65/7.16/4.52	73.74/7.24/4.51	1568	1419	487
4	$Co(C_{19}H_{22}NO)_2$	64	73.65/7.16/4.52	73.59/7.17/4.54	1561	1415	489
5	$Co(C_{21}H_{26}NO)_2$	65	74.64/7.76/4.15	74.68/7.80/4.14	1564	1422	486
6	$Co(C_{23}H_{30}NO)_2$	65	75.49/8.26/3.83	75.46/8.29/3.80	1563	1415	488

[a] All complexes are off white colored crystals.
[b] The values are induced by metal to ligand charge transfer (MLCT).

Table 2
Results of 1,3-butadiene polymerizations over various cobalt salicylaldimine complexes combined with ethylaluminum sesquichloride (EAS). Polymerization conditions: catalyst = 2.8 μmol, [EAS]/[Co] = 200, [BD] = 0.7 M, toluene = 20 mL, time = 10 min and temperature = 30 °C

Run no.	Catalyst	Yield (%)	M_n[a]	M_w/M_n[a]	Triad fractions (%)[b]		
					1,4-*cis*	1,4-*trans*	1,2-
1	**1**	57	34,500	1.29	98.03	1.86	0.11
2	**2**	56	44,500	1.66	97.14	1.73	1.13
3	**3**	55	32,600	1.68	94.98	2.21	2.81
4	**4**	52	41,200	1.71	96.70	2.11	1.19
5	**5**	51	33,900	2.36	96.19	2.16	1.65
6	**6**	47	37,200	1.68	94.31	2.32	3.37

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

Table 3
Results of 1,3-butadiene (BD) polymerizations over cobalt salicylaldimine (**1**)/ethylaluminum sesquichloride (EAS) catalyst at various BD concentrations. Polymerization conditions: catalyst = 2.8 μmol, [EAS]/[Co] = 200, toluene = 20 mL, time = 10 min and temperature = 30 °C

Run no,	[*BD*] (M)	Yield (%)	M_n[a]	M_w/M_n[a]	Triad fractions[b] (%)		
					1,4-*cis*	1,4-*trans*	1,2-
1	0.2	29	23,500	1.80	94.66	3.66	1.68
2	0.3	42	23,800	1.82	94.11	3.34	2.55
3	0.4	47	25,400	1.93	95.81	2.81	1.38
4	0.5	50	23,400	1.73	96.66	1.95	1.39
5	0.6	58	35,000	1.81	96.93	1.66	1.01
6	0.7	57	34,500	1.29	98.03	1.86	0.11

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

molecular weight distributions, 1,4-*cis* content, 1,4-*trans* content and 1,2 content of polymers. Percentage error for all these parameters are with in the range of ±0.9.

3. Results and discussion

3.1. Catalyst preparation and BD polymerizations

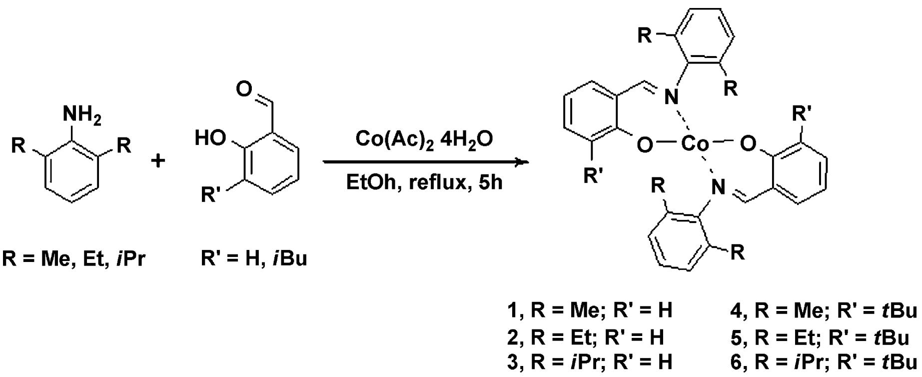
Careful designing of ligands, including selection of atoms, its placing in overall geometry of the ligand, different substituents in ligands and their positioning, have an important role in determining the activity of the catalyst and the property of resulting polymer in olefin and diene polymerizations. By this predesigning, the stereo- and regioselectivity of insertion of the monomer could be tuned. Such factors influencing the microstructure of polymers have been extensively investigated by many groups recently [1–7,11–19].

As a means of investigating the effect of catalyst structure on activity and polymer microstructure, we prepared a series of cobalt salicylaldimine complexes with changes in the bulkiness of *ortho* substituents of aniline and phenol moieties (Scheme 1). 2-((2,6-Dialkylphenylimino)methyl)phenol (alkyl = methyl, ethyl and isopropyl) and 2-tert-butyl-6-((2,6-dialkylphenylimino)methyl)phenol ligands, synthesized by condensing 2-hydroxybenzaldehyde or 3-tert-butyl-2-hydroxybenzaldehyde with 2,6-dialkylaniline, in equimolar ratio, on refluxing with cobalt acetate tetrahydrate in ethanol yielded cobalt complexes **1**–**6**. One-shot synthetic method has been adopted in order to

Table 4
Results of 1,3-butadiene (BD) polymerizations over cobalt salicylaldimine complexes (**1** and **4**)/ethylaluminum sesquichloride (EAS) catalyst at different temperatures. Polymerization conditions: catalyst = 2.8 μmol, [EAS]/[Co] = 200, [BD] = 0.7 M, toluene = 20 mL and time = 10 min

Run no.	Catalyst	Temp.[a] (°C)	Yield (%)	M_n[b]	M_w/M_n[b]	Triad Fractions[c] (%)		
						1,4-*cis*	1,4-*trans*	1,2-
1	**1**	70	63	36,000	2.39	87.95	10.33	1.72
2	**4**	70	56	36,700	1.63	83.88	10.86	5.26
3	**1**	50	64	41,500	2.06	94.06	2.84	3.10
4	**4**	50	58	40,000	2.46	91.18	6.71	2.11
5	**1**	30	57	44,500	1.29	98.03	1.86	0.11
6	**4**	30	52	41,200	1.71	96.70	2.11	1.19

[a] Polymerizations at 0, 10 and 20 °C give only negligible activities.
[b] Measured by GPC.
[c] Measured by ^{1}H and ^{13}C NMR spectroscopies.



Scheme 1. Synthesis of cobalt(II) salicylaldimine complexes in one-pot protocol.

avoid ligand purification step and hence to make the process more convenient. All compounds were obtained in high yields over 60% (see Table 1). On the basis of elemental analysis, the metal to ligand stoichiometry of 1:2 has been proposed for Co(II) complexes. The proposed structure (Fig. 1) for these complexes has the support of IR spectra.

In IR spectra of the cobalt complexes, absence of any absorption bands around 3000–3100 cm^{-1} region and around 3300–3400 cm^{-1} assigned to phenolic groups indicates that a metal–oxygen bond has removed hydrogen from the hydroxyl groups. A strong band around 1561–1568 cm^{-1} region in these complexes confirms formation of coordinative bonds from the imine moieties to the metal. Also the strong band at 1415–1422 cm^{-1} appeared for all complexes assigned to the ν(C–O) mode of coordinated salicylic C–O bond. Coordination mode of the ligands was further supported by the bands appearing in the 424–628 cm^{-1} region, characteristic of Co–N and Co–O bonding vibrations [20]. From the elemental analysis and infrared studies, it has been concluded that the ligand has linked through phenolic oxygen and coordinated through imine nitrogen behaving as a bidentate ligand. Fig. 1 shows geometry optimized structures of cobalt complexes. Geometry optimizations were carried out using the Hyperchem 7.5 package running on a Windows PC workstation. Geometry optimizations were done at the Restricted Hartree–Fock level. Polak–Rebiere algorithm was used for the optimization. Optimization of structure built in the Hyperchem program calculates the possible structure of the cobalt complexes where the net forces on each atom are reduced to zero. We assume the initial structures that the strong Co–O bonds and the weak Co–N bonds are *trans* to each other.

Solution polymerizations of 1,3-BD were carried out in toluene at 30 °C by combining the cobalt complexes with EAS ([EAS]/[Co] = 200). As summarized in Table 2, all cobalt

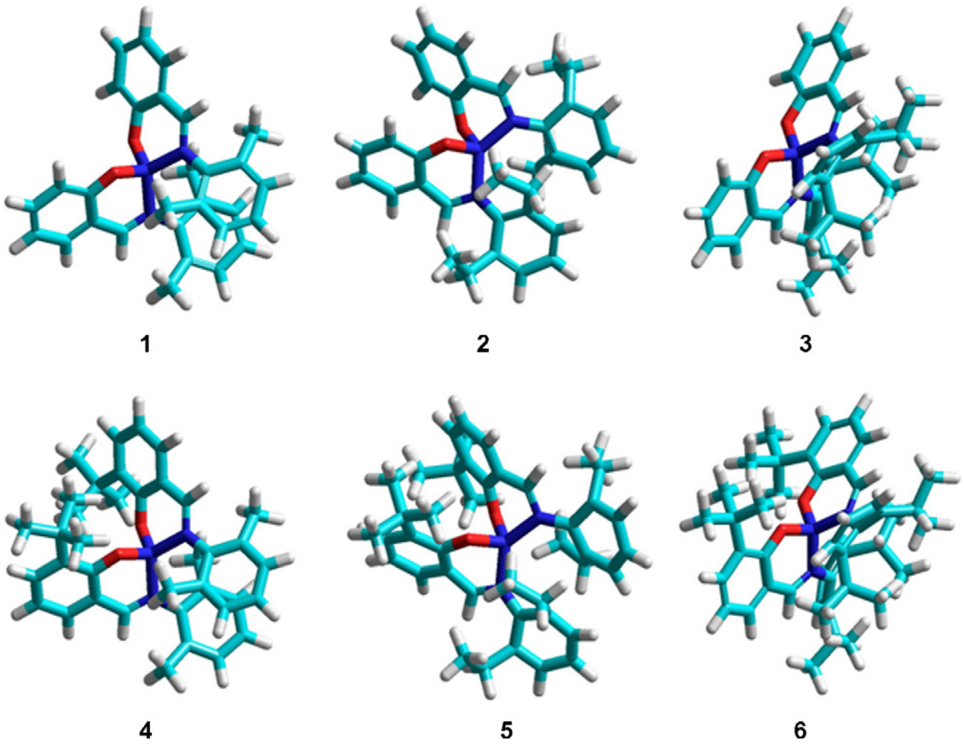


Fig. 1. Optimized geometry of cobalt(II) salicylaldimine complexes.

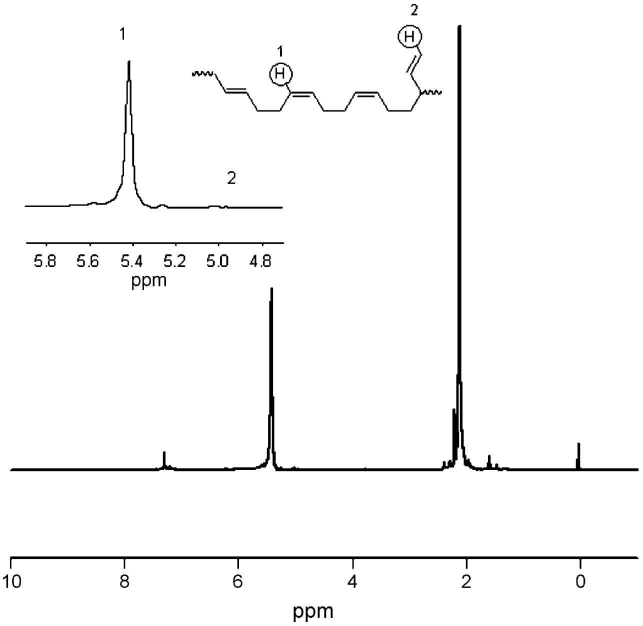


Fig. 2. ^{1}H NMR spectrum of the polybutadiene (run no. 4 in Table 2) produced by (2,6-dimethylaryl-N=C-3-*t*-butylaryl-O)$_2$Co complex (**4**)/EAS catalyst.

complexes show very high activity, yield from 47% to 57% within 10 min. Note that we stopped polymerizations in 10 min for facile agitation. As the steric bulk of the complex increases from **1** to **6**, the yield decreases monotonously. All PBDs obtained have moderate MW (M_n = 22,600–38,200) with narrow MWD (1.29–2.36).

The stereoregularity of the resulting polymers was investigated by both ^{1}H NMR and ^{13}C NMR spectroscopies. Figs. 2 and 3 show ^{1}H NMR and ^{13}C NMR spectra, respectively, of PBD obtained by **4**/EAS catalyst (Entry No. 4 in Table 2). The microstructure was elucidated from the spectra in accordance with the reported literatures [5,21–23]. It is evident that all catalysts yield PBDs of highly 1,4-*cis* structure. Investigating complex **1** to **3**, bearing nonsubstituted phenoxy ligand, the *cis* amount of the polymer decreases as the steric bulk increases, even if the difference is not so remarkable. The same trend is observed for complex **4** to **6**, bearing 2-tert-butyl substituted phenoxy ligand.

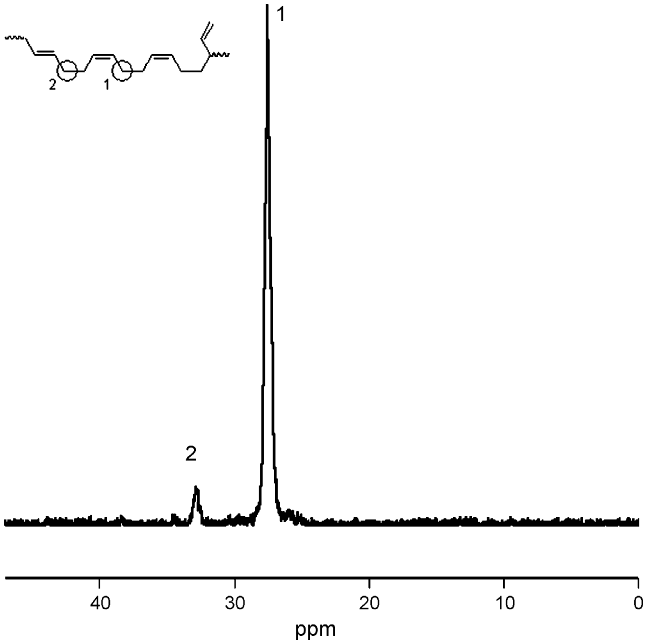


Fig. 3. ^{13}C NMR spectrum of the polybutadiene (run no. 4 in Table 2) produced by (2,6-dimethylaryl-N=C-3-*t*-butylaryl-O)$_2$Co complex (**4**)/EAS catalyst.

The narrow MWD values of PBD obtained by the present catalyst system may be the outcome of living nature of active center. In order to check this point, a series of polymerizations were carried out with **1**/EAS catalyst, which yields PBD with the lowest MWD (1.29), by changing BD concentration from 0.2 to 0.7 M. The results of polymerizations are summarized in Table 3. Even if yield increases as BD concentration increases, it is hard to say **1**/EAS catalyst shows living character, especially considering BD concentration to M_n relationship. A narrow MWD is an unique feature of PBD products of the cobalt complex based catalysts. The MWD value lower than 2 is possibly indicative of uniform active species present in the polymerization system. The molecular weight of a PBD (here defined as the average degree of polymerization, P_n) made with catalysts of uniform active sites can be given by

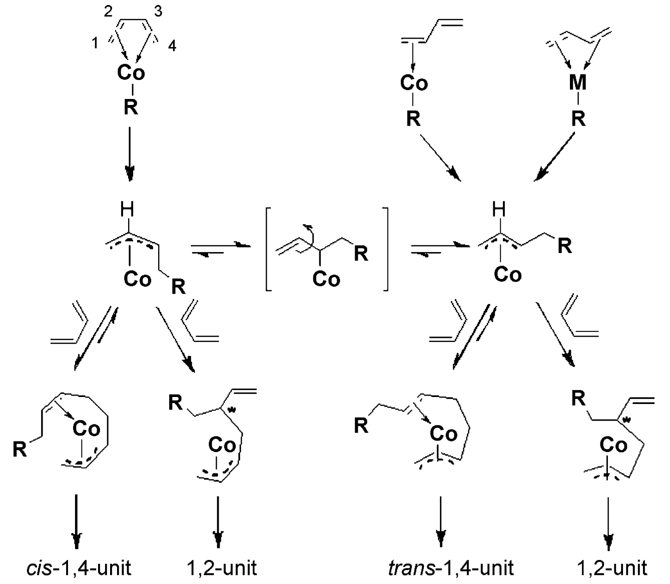
$$P_n = \frac{\sum R_p}{\sum R_r}$$

That is, in terms of reaction rates, the MW of PBDs is given by the ratio between the overall rate of propagation (R_p) and the sum of all rates of chain release (R_r) reactions (usually referred to as termination and/or transfer reactions): this means that the MW is dependent on the type of catalyst and the kinetics of the process, that is, the polymerization parameters (polymerization temperature, monomer concentration, catalyst/cocatalyst ratio). It is also interesting to note that the stereospecificity of transition metal catalyzed polymerizations can also be changed according to polymerization conditions. As shown in Table 3, 1,4-*cis* content of PBD increase from 94.7% for [BD] = 0.2 M to 98.0% for [BD] = 0.7 M.

A series of polymerizations were performed by using **1**/EAS and **4**/EAS catalysts at a temperature between 10 and 70 °C (Table 4). Even if only negligible activities are recorded at temperatures lower than 20 °C, polymerization yield increases as polymerization temperature increases above 30 °C (see Table 4). The MW of PBD decreases monotonously as the polymerization temperature increases for both catalysts due to the activated termination reaction, that is, higher rate of chain release reaction, at higher temperature. The 1,4-*cis* amount of PBD decreases as the temperature increases for both catalysts.

3.2. Mechanism for stereochemical control

In the conjugated diene polymerizations, all suggested explanations for stereochemical control of polymer chain has been around the way in which 1,3-BD monomer complexes at the metal center. At the growth step, stereoregulation may be occurring on the moment of diolefin complexation to the metal



Scheme 2. Proposed mechanism for stereochemical control in butadiene polymerization by Co(II) complex.

center during the formation of transition state or after the diene has been inserted into the transition metal–carbon bond through σ- or π-allyl-type interactions [11].

Coordination of BD molecule to transition metal atom favors a *cis*-1,4-complexing mode when radius of the metal is not favorable for coordination at two coordination positions of the atom. Cobalt has this correct spatial arrangement and orbital overlap favoring coordination at two positions [11]. Regardless of the central metal atom, virtually one and the same polymerization mechanism were proposed for nearly all catalytic species [1,24]. As illustrated in Scheme 2 for the polymerization mechanism over cobalt complex, bonding of the end unit of growing polymer chain to the metal center is π-allylic type and hence different insertion pathways are possible.

Two reactive sites C1 and C3 are possible for the allylic units and thus enables 1,4- and 1,2-insertion of the diene coordinated to the metal center (chemoselectivity). While coordinating to metal center, the terminal allyl unit of the polymer chain can be in *anti* or *syn* conformation. The *anti* and *syn* coordinated end units have quite an important role in determining structure of the polymer. The *anti* conformer results in *cis*-1,4-PBD, while the *syn* conformer causes *trans*-1,4-PBD formation. The *syn* form is expected to be thermodynamically preferred for butenyl groups not substituted at the C2 atom [1]. The *anti* isomer can be preferred for kinetic reasons, because the more stable *cis*-η^4-coordinated ligands yield the *anti* form after insertion. The less stable *trans*-η^2- or *trans*-η^4-coordinated ligands yield a thermodynamically more stable *syn*-allyl isomer.

Decrease in the positive charge on the Co metal center resulting from a electron donating effect imposed by the substituents on ligands increases the probability of diene coordination through one double bonds rather than a coordination through two double bonds, which results a decrease in 1,4-*cis* inserted product as shown in Table 2. Another factor influencing the stereoregularity may be the bulkiness of substituents. In the insertion mechanism an *anti–syn* isomerization via η^1-allyl coordination through a π-σ rearrangement is possible and it makes the reaction pattern considerably complicated. When the insertion step is quicker than *anti–syn* rearrangement, *cis* polymer from the *anti* isomer predominates. When observed through the precatalyst from **1** to **6**, one can find that the increase in bulkiness of the substituents increases the steric crowding at the metal center and it makes the insertion step slower. Hence the *anti–syn* rearrangement favors less amount of *anti* form in the system, which reduces the amount of polymers with *cis* orientation.

A significant effect of monomer concentration is also observed (Table 3), i.e. *cis* content increases with monomer concentration, while *trans* content decreases. No significant influence of monomer concentration on the 1,2-content is observed. This is in accordance with the general concentration effect observed with titanium, cobalt and nickel complexes [1] that on high diene concentration there may not be enough time for *anti–syn* rearrangement and hence the kinetic product, the *cis* polymer, will dominate. On the other hand, at lower diene concentration the polymerization rate will be lower and therefore increases favorability of *anti–syn* isomerization leading to relatively higher *trans* polymer.

3.3. UV–vis spectroscopic study of the cobalt(II) salicylaldimine complex/EAS system

The elucidation of active species for olefin polymerizations by many early and late metal catalysts has been made experimentally and theoretically [25–31]. The presence of chromophoric aromatic ligands directly attached to the cobalt metal allows an investigation by UV/visible spectroscopy of cobalt salicylaldimine complexes/EAS systems in conditions

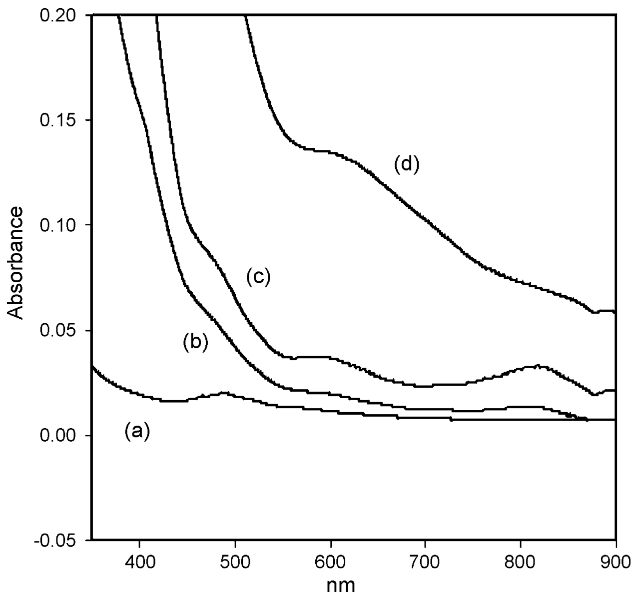
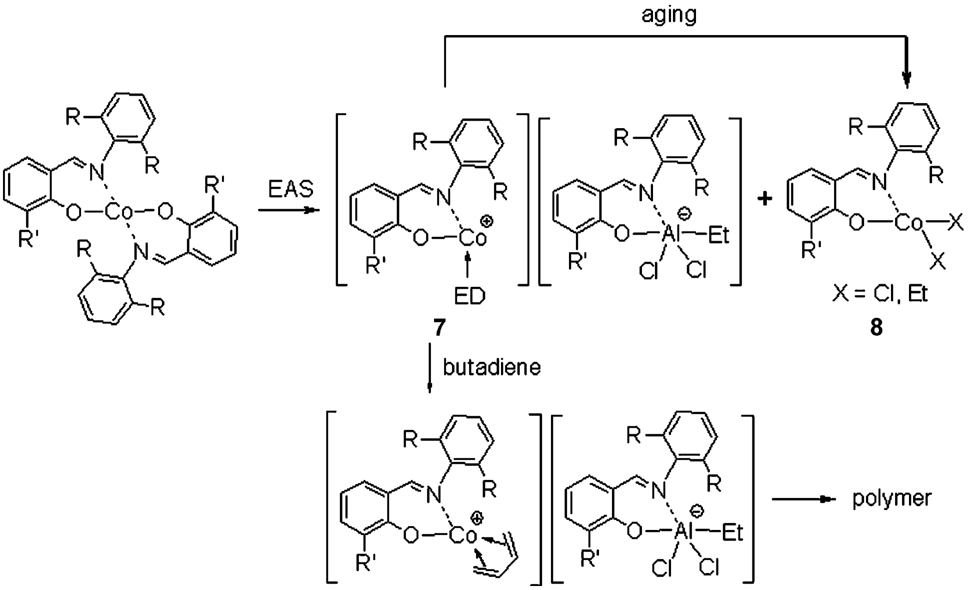


Fig. 4. UV-visible spectra of (2,6-dimethylaryl-N=C-3-*t*-butylaryl-O)$_2$Co complex (**4**) and **4**/ethylaluminu sequichloride (EAS) catalyst in toluene solution: (a) cobalt complex **4** alone, (b) **4**/EAS mixture with 300 equiv. of EAS, (c) **4**/EAS mixture with 400 equiv. of EAS and (d) **4**/EAS mixture with 400 equiv. of EAS after aging the mixture for 1 h at 70 °C.



Scheme 3. Formation of active cobalt species by the reaction of cobalt(II) salicylaldimine complex with ethylaluminum sesquichloride (EAS).

much closer to the polymerization, i.e. lower metal concentration and high [EAS]/[Co] ratios (up to several hundreds). The formation of various types of cobalt species upon incremental addition of EAS has been identified by this last technique. In fact, recent attempts on UV/visible spectroscopic investigations of several zirconocene/MAO systems [26–30] and α-diimine-[*N*,*N*]$NiBr_2$/MAO system [31] for olefin polymerizations have been contributed much to understand the successive elementary steps yielding cationic active species in zirconocenes and nickel α-diimine systems. We have extended this study to characterize the elementary steps leading to the formation of active species in BD polymerizations by cobalt salicylaldimine/EAS system in toluene medium.

As can be seen in Fig. 4, the complex (**4**) alone shows an absorption maximum around 500 nm and it gives no other characteristic UV–vis absorption bands between 400 and 900 nm. Addition of various amounts of EAS ([EAS]/[**4**] = 10–400) to the toluene solution of **4** results in the formation of two new absorption bands at around 600 and 800 nm. We showed here only part of the spectra, that is when [EAS]/[**4**] = 300 and 400, for convenient differentiation of the bands. Addition of BD monomer to the UV/visible cell containing mixtures with various [EAS]/[**4**] ratios yields PBD in a few minutes, demonstrating one or both of the two new bands are attributed to the active species. In order to check this point, UV-visible spectrum was obtained after aging the **4**/EAS ([EAS]/[Co] = 400) mixture for an hour at 70 °C (Fig. 4(d)). The band at around 800 nm becomes almost disappeared and the band at around 600 nm becomes stronger. Interestingly this aged mixture gave no polymer by the addition of BD. These results demonstrate that the absorption band around 800 nm is assigned to be active species of the system.

According to the recent study [32] to elucidate the nature of the active species in bis(imino)pyridyl cobalt ethylene polymerization catalyst, the active species is not the anticipated cobalt(II) alkyl cation. It was found that $LCo(II)Cl_2$ (L = bis(imino)pyridyl ligand) transferred to LCo(I)Me species upon alkylation by strong Lewis acid (e.g. MAO) and then to Co(I) cationic species that contains no cobalt–C bond. Ethylene monomer coordinates to this cationic species to yield polyethylene. If we apply this study to cobalt salicylaldimine complexes/EAS systems considering polymerization results obtained in this study, it is proposed that the EAS cocatalyst appears to perform two functions: (i) to reduce the Co(II) precatalyst to Co(I) cations by abstracting one of the two bidentate ligands, and (ii) to enhance the stability of the catalyst, and/or the rate of polymerization. Scheme 3 shows the most plausible procedures of the formation of Co(I) active species in BD polymerization. Possibly the UV-visible band around 800 nm (Fig. 4) is assigned to active species such as **7** that is stabilized by anionic aluminum moiety. Some types of electron donors existed in the system such as solvent and nitrogen gas may coordinate to the Co cations before monomer is added. Together with the active cationic Co(I) species, inactive species such as Co(III) complex (**8**) can also be formed by the reaction with excess amount (e.g. [EAS]/[Co] = 400) of aluminum cocatalyst. Aging of active **7** species at high temperature can also give this kind of stable inactive species. Investigation into these possibilities, and other aspects of the chemistry of the cobalt system, will be reported in due course.

4. Conclusions

Exploiting the recent developments and knowledge on ligand oriented postmetallocene catalyst design, we prepared a group of Co(II) salicylaldimine complexes by modifying the steric bulk imposed to the metal center. Combining ethylaluminum sesquichloride, these complexes yield highly active butadiene polymerization catalysts and the resulting polymers are characterized by an obtrusive microstructure with a fondness towards *cis* insertion (>94.3%). Studies were oriented around the ability of the catalyst to produce polymers with very high *cis* content. Changes in steric bulk at the active center by the variation of alkyl substituents on the ligand environment, monomer concentration and polymerization temperature found to affect the *cis* content of the resulting polymers, that is, the *cis* content increases with the decrease of the steric bulk and polymerization temperature, and with the increase of monomer concentration. We also investigated the elementary reactions involved in the catalytic activation process of cobalt(II) complex in conjunction with EAS, by utilizing UV-visible spectroscopy.

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