



Highly Stereospecific Polymerizations of 1,3-Butadiene with Cobalt(II) Pyridyl Bis(imine) Complexes

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Abstract: A series of prototypical Co(II)-based pyridyl bis(imine) complexes {[2-(ArN=C(Me))₂C₅H₃N]CoCl₂} (Ar = 2,6-C₆H₃Me₂, 2,5-C₆H₃Me₂, 2,4-C₆H₃Me₂, 2,3-C₆H₃Me₂) bearing two methyl substituents on each imine aryl group are studied as precatalysts for the homopolymerization of 1,3-butadiene. They showed very high polymerization activities associated with ethylaluminum sesquichloride (EAS) as a cocatalyst. The Co(II) catalysts containing less hindered pyridyl bis(imine) ligands, say [2-(2,3-C₆H₃Me₂N=C(Me))₂C₅H₃N]CoCl₂ complex, showed highest activity to give high molecular weight polymers. All catalysts yielded *cis*-1,4-polybutadienes up to 96.4% with *cis*-1,4 regular structure.

Introduction

Stereo- and regiospecific polymerization of 1,3-butadiene, i.e. 1,4-*cis*, 1,4-*trans*, 1,2-syndiotactic, or 1,2-isotactic polymerization, is very important both academic and industrial fields. In particular, selective 1,4-*cis*-specific polymerization has attracted much attention, because the resulting polybutadiene exhibits excellent elastic properties and is useful as synthetic rubber [1,2]. In 1954, it was discovered that the catalyst system, TiCl₄/AlR₃ polymerizes isoprene into *cis*-1,4-polymer [1-3]. Later it has been found that catalyst systems composed of a Ti, Co, Ni, V, or rare earth metal compound and an organoaluminum give *cis*-1,4-polybutadiene [1-3]. There has been recent interest in the use of soluble transition metal catalysts such as titanocene/methylalumoxane (MAO) catalysts [4], Ti(O^{*i*}Pr)₄/MAO [5], Ti(CH₂Ph)₄/MAO [6], Ni(acac)₂/MAO [7], and Ni(oct)₂/AlF₃/AlEt₃ [8] for 1,4-polymerizations of isoprene and 1,3-butadiene (BD) to obtain high molecular weight (MW) polymers with low polydispersities as efficient low-cost materials for improved synthetic rubber. The mechanism of diolefin polymerizations with various transition metal initiator systems was deeply studied and reviewed by Porri and coworkers [3].

Recently new cationic tridentate Co(II)-based pyridyl bis(imine) catalysts were synthesized by Brookhart *et al.* and widely used for the polymerization of olefins [9,10]. Some distinguished features of the pyridyl bis(imine) ligand catalysts are their high electrophilicity, cationic metal centre and the use of sterically bulky pyridyl bis(imine) ligands. This type of catalysts is characterized by reduced oxophilicity and thus a higher tolerance for functional groups. Cobalt-based homogeneous catalyst systems are attractive catalysts from the points of not only polymerization capabilities for versatile monomers such as cyclic olefins, ethylene or 1-olefins, styrene and its derivatives, conjugated dienes, and methacrylic monomers but also the advantage to require a lesser amount of MAO as a cocatalyst to reach high activity as compared to

the metallocene catalysts for the polymerization of olefins [10]. It has been found that the Co(II)-based pyridyl bis(imine)/MAO was the effective catalyst for the polymerizations of polar monomers such as methyl methacrylate [11] and vinyl ether [12].

The large number of possible variations in these Co(II)-based pyridyl bis(imine) catalyst systems allow for more specifically designed catalysts, possibly selective for the optimized polymerizations of desired conjugated dienes as well. As a result, we decided to investigate efficient catalysis using Co(II)-based pyridyl bis(imine) complexes for polymerizations of BD. In this paper, we report our preliminary results obtained in the polymerization of BD promoted by a series of prototypical Co(II)-based pyridyl bis(imine) complexes (Fig. 1) in the presence of ethylaluminum sesquichloride (EAS) cocatalyst.

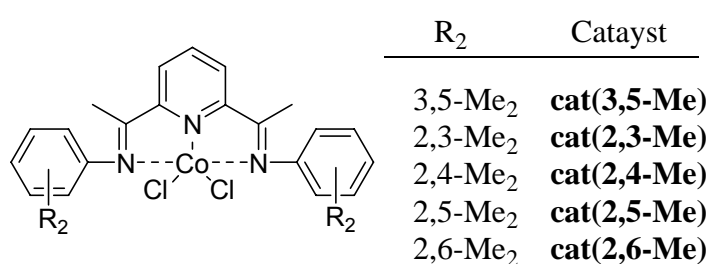


Fig. 1. The structure of bis(imino)pyridyl cobalt(II) precatalysts utilized in this study.

Results and discussion

Solution polymerizations of BD were carried out in a stirred 40 mL glass reactor by using Co(II)-based pyridyl bis(imine) complexes (Fig. 1) combined with EAS. Polymerization time was controlled to 40 minutes for a facile agitation. The results of the polymerizations are summarized in Tab. 1. The Co(II) precatalysts employed were prepared by modifying the position of two methyl substituents on aryl rings, resulting in change of steric bulk of the catalyst. According to the previous reports [9, 10] on the ethylene polymerizations with similar precatalysts combined with MAO, the protective bulk of the *ortho* substituents above and below the metal centre is critical to achieve high MW polymer in olefin polymerizations. As a result **cat(2,3-Me)**, **cat(2,4-Me)**, **cat(2,5-Me)**, and **cat(3,5-Me)** catalysts yielded oligomer products in ethylene polymerization, while **cat(2,6-Me)** catalyst gave polyethylene with low molecular weight [9, 10]. In this sense, it is interesting to investigate BD polymerizations with the same catalysts in order to get an insight on a mechanistic difference between olefin and conjugated diene polymerizations.

The **cat(2,3-Me)** containing 2,3-methyl substituents in the aryl rings showed the highest activity in 40 min of polymerization (Tab. 1). The activity decreases in order of **cat(2,3-Me) > cat(2,4-Me) > cat(2,5-Me) > cat(3,5-Me) > cat(2,6-Me)**. It is surprising to note that **cat(2,6-Me)**, which shows very high activity in ethylene polymerizations up to 11 kg mmol⁻¹h⁻¹bar⁻¹ [10], shows the lowest activity. It demonstrates that the propagation rate of active cobalt species-BD coordinated complexes is different from that of active species-ethylene coordinated species. The BD monomer is differentiated from ethylene monomer in that it contains conjugated diene with relatively bulkier structure than ethylene. In this sense the electronic and steric

environments of the active species imposed by growing polymer chain should be quite different each other. These made the catalytic activities and the molecular weights resulting from butadiene polymerizations and from ethylene polymerizations with the same catalyst systems completely different.

Tab. 1. Solution polymerization results for butadiene using cobalt(II) pyridyl bis(imine) complexes. Polymerization conditions: [BD]= 1 mol/L; [Cat.] = 2.00×10^{-4} mol/L; [EAS]/[Co] = 100; toluene = 20 mL; polymerization temperature = 30°C.

Entry No.	Catalyst	Time (min)	Yield (%) ^a	M_n ($\times 10^{-5}$) ^b	M_w/M_n ^b	Triad fractions c (%) ^c		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2
1	cat(3,5-Me)	40	10.71	1.57	1.21	97.73	1.28	0.99
2	cat(2,3-Me)	40	25.70	1.34	1.24	96.64	2.43	0.93
3	cat(2,4-Me)	40	21.83	1.28	1.17	98.19	1.17	0.64
3' ^d	cat(2,4-Me)	48h	16.1	1.07	1.37	95.78	2.4	1.82
4	cat(2,5-Me)	40	16.52	1.45	1.29	98.62	0.92	0.46
5	cat(2,6-Me)	40	5.65	1.22	1.24	97.29	2.18	0.53
6	cat(2,4-Me)	10	0.99	0.57	1.29	98.63	0.65	0.72
7	cat(2,4-Me)	15	1.86	1.20	1.11	97.99	1.23	0.78
8	cat(2,4-Me)	30	17.10	1.24	1.19	97.30	1.97	0.73
9	cat(2,4-Me)	90	59.34	1.62	1.24	96.48	2.63	0.89

^a Yield defined a mass of dry polymer recovered/mass of monomer used.

^b Determined by GPC.

^c Measured by ¹H-NMR spectra and ¹³C-NMR.

^d Polymerization conditions are the same as Entry No. 3 except [MAO]/[Co] = 1000 and polymerization time = 48 h.

As indicated in Tab. 1, the molecular weights of all polybutadienes are high (say, $M_n = 157,000$ for **cat(3,5-Me)**), even though no clear trends can be found according to the position of the methyl substituents. It is very interesting to note that the same catalyst (**cat(3,5-Me)**) yielded only oligomers with 1-butene as a major composition in ethylene polymerizations [9, 10, 13]. These results demonstrate that increase of steric bulk of the *ortho* substituents of the N-aryl ring is not a necessary condition to achieve high MW polymers in BD polymerizations.

In order to check the living character of active species, a series of polymerizations were performed by using **cat(2,4-Me)**/EAS system by changing the time from 10 to 90 min (see Entry No. 3 and from No. 6 to 9 in Tab. 1). Both activity and molecular weight did not linearly increase according to time, demonstrating that the present catalyst systems do not have living character, while they show polymerization behaviours which can be generally found in single-site coordination catalyst systems.

Narrow MWD values reported in Tab. 1 were obtained at rather low monomer conversions (polymer yields). In order to investigate the effect of monomer concentration on the molecular weight of polymer, a series of polymerizations were carried out for 90 min at 30 °C, by changing the monomer concentration from 0.2 to

3.0 M. The polymer yield monotonously increased as the monomer concentration increases; i.e. the yields were 47.2, 52.8, 59.3, 64.5, and 73.8 % at monomer concentrations of 0.2, 0.5, 1.0, 2.0, and 3.0 M, respectively. Fig. 2 shows the variations of M_n and MWD according to monomer concentration. The molecular weight was not linearly proportional to the monomer concentration and the MWD values are kept between 1.2 and 1.4. The investigation of the low MWD values without any proofs of living nature of the system is a good subject of further study.

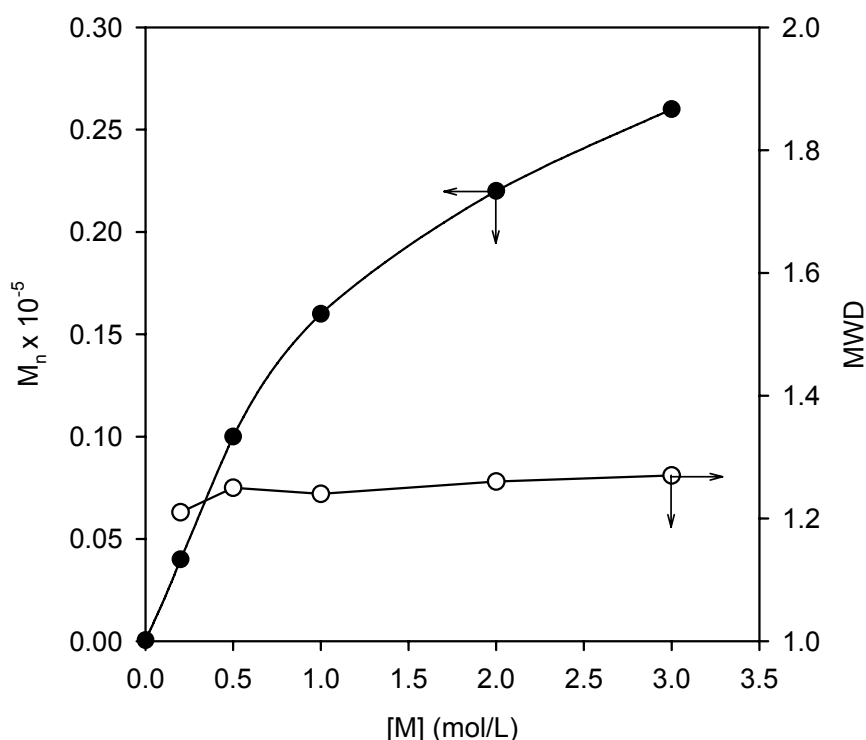


Fig. 2. The variation of molecular weight and its distribution according to monomer concentration in butadiene polymerizations using cobalt(II) pyridyl bis(imine) complexes [**cat(2,4-Me)**] combined with EAS. Polymerization conditions: [Cat.] = 2.00×10^{-4} mol/L; [EAS]/[Co] = 100; toluene = 20 mL; polymerization temperature = 30 °C; time = 90 min.

Polymerization temperature is one of the most important parameters in both scientific and technological senses. A series of polymerizations were carried out with **cat(2,4-Me)**/EAS system over a temperature range between 10 and 70 °C and the results are summarized in Tab. 2. The catalyst system showed only negligible activity at 10 °C and the highest activity at 50 °C. As the temperature increase, the MW decreases monotonously, with MWD remaining narrow. In addition *1,4-cis* addition decreases as the temperature increases, but still is highly stereospecific. It is also interesting to note the difference between BD and ethylene polymerizations. In the latter case with the same catalyst system, it showed high activity at 10 °C but negligible activity at 70 °C [13]. In addition the **cat(2,4-Me)** catalyst showed very high activity when it is associated with MAO in ethylene polymerizations [9, 10, 13]; however, the same system showed very low activity in butadiene polymerization (see Entry no. 3' in Tab. 1). These results indicate that the bulkiness of monomer and its resulting coordinating species and cocatalyst structure influence the propagation rate.

Tab. 2. Effect of temperature on solution polymerization of butadiene using cobalt(II) pyridyl bis(imine) complex. Polymerization conditions: [1,3-butadiene]= 1 mol/L; [Cat.] = 2.00×10^{-4} mol/L; [EAS]/[Co] = 100; toluene = 20 mL; polymerization time = 40 min.

Entry	Catalyst	Temp (°C)	Yield (%) ^a	M_n ($\times 10^{-5}$) ^b	M_w/M_n ^b	Triad fractions ^c (%)		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2
1 ^d	cat(2,4-Me)	10	nil	-	-	-	-	-
2	cat(2,4-Me)	30	21.83	1.28	1.17	98.19	1.17	0.64
3	cat(2,4-Me)	50	41.15	1.26	1.16	97.49	1.53	0.98
4	cat(2,4-Me)	70	20.42	0.82	1.19	92.44	6.46	1.10

^a) Yield defined a mass of dry polymer recovered/mass of monomer used.

^b) Determined by GPC.

^c) Measured by ¹H-NMR spectra and ¹³C-NMR.

^d) Negligible activity at polymerization conditions of the present study.

In 1995, a report by Brookhart and co-workers on the discovery of a new class of catalysts for the polymerization of ethylene and α -olefins was received with strong interest in academia and industry alike [9, 10]. Brookhart and co-workers findings have resulted in a strongly increased interest in late transition metal olefin polymerization catalysis, and spurred an intense search for other suitable ligand structures. Subsequently, three different research groups (Brookhart, Gibson, and Bennett of DuPont) independently reported cationic iron and cobalt catalyst systems of pyridyl bis(imine) ligands for the polymerization of ethylene to highly linear, crystalline high-density polyethylene (HDPE) [14, 15]. Astounding rates of up to 10^7 TO h⁻¹ (at 40 bar ethylene pressure) have been reported for the iron catalysts. The typical relative ease of preparation for many of the late transition metal catalyst systems highlighted is exemplified by the preparation of the iron and cobalt catalysts. In analogy to nickel(II) and palladium(II) complexes of bulky substituted diimine ligands, the steric bulk of the *ortho*-aryl substituents retards chain transfer. Reducing the steric bulk of the *ortho*-aryl substituents R in the iron complexes again yields catalysts for ethylene oligomerization [15(d), (e), 16]. Again extremely high activities of up to 10^8 TO h⁻¹ for formation of >99% linear α -olefins were observed, far exceeding the activities reported for SHOP catalysts. Ethylene oligomerizations by using Co(II) complexes bearing 3,5-dimethyl substituted pyridyl bis(imine) ligand (**cat(3,5-Me)**) yielded predominantly 1-butene with very high activity [13,16].

Whereas these catalysts exhibit excellent properties as described, one limitation is their relatively high sensitivity to temperature. Increased polymerization temperatures result in decreased molecular weights. Catalysts are stable for hours at 30 °C, but the catalysts decompose rapidly at 50 °C for Fe(II)- and Co(II)-based pyridyl bis(imine) systems [9, 13, 15-17]. However, comparing to ethylene polymerizations by using the same catalysts investigated in this study, butadiene polymerizations are characterized by the fact that (1) all catalysts combined with EAS yield higher activity at higher polymerization temperatures, (2) catalyst (**cat(3,5-Me)**) bearing no protective bulk of the *ortho* substituents shows high activity and affords high molecular weight polymers even at high temperature (say 70 °C), (3) polymerization

temperature is not a critical factor resulting in increased chain transfer, and (4) MAO is not an effective coactivator.

Considering the results obtained in this study and the previous reports [9, 15-17] obtained with various catalyst systems, in ethylene polymerizations by Co(II)-based pyridyl bis(imine) catalysts (see **A** in Fig. 3), the aryl groups are roughly perpendicular to the coordination plane so the bulky substituents on the aryls are positioned at the axial directions to retard associative chain transfer reactions. At elevated temperature, the aryl groups may freely rotate away from the perpendicular orientation, resulting in increased associative chain transfers and a resulting decrease in molecular weight of the PE [18]. It is postulated that in butadiene polymerizations by the same catalysts (**B** in Fig. 3), both the mode of monomer coordination to the catalyst species and the structure of growing chain ends are different from those in ethylene polymerization, resulting in the stereoregularity of diene polymers. The structure **B** in Fig. 3 shows the last polymerized unit (in the η^1 -allylic form), the cobalt complex and the incoming monomer. When a cisoid monomer coordinates to a cobalt with two double bond, the *anti* π -allyl structure results [3].

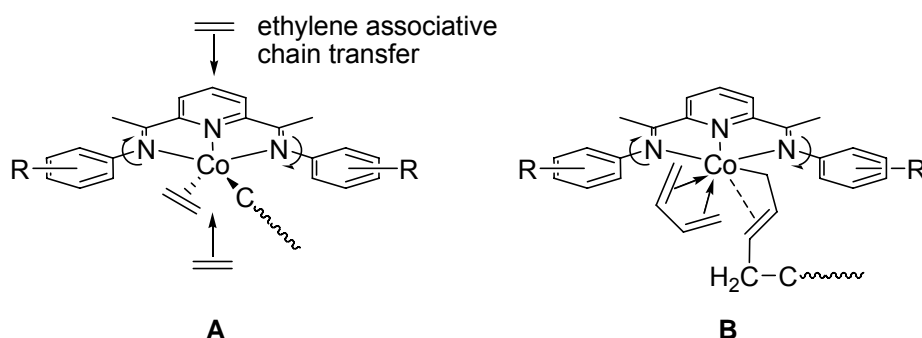


Fig. 3. Comparison of the coordination of ethylene (**A**) with BD (**B**) to cobalt atom.

Even though detailed mechanistic studies are needed to draw a conclusion, if the monomer coordinates with Co-C bond of the complex and 1 and 4 carbon atoms of the diene being involved, all units of the forming chain will have a 1,4 (*cis* or *trans*) configuration, as shown in Fig. 4 [3]. This mode of coordination may block the axial faces of the metal leaving only two *cis*-coordination sites for monomer entry and polymer growth. The crowded coordination mode prohibits free rotation of the aryl–nitrogen bonds, which should allow the catalyst to make high molecular weight polymers at elevated temperature. Negligible activities for butadiene polymerizations at low temperature seem that there is no sufficient room for cisoid butadiene to be coordinated due to the lack of rotational flexibility.

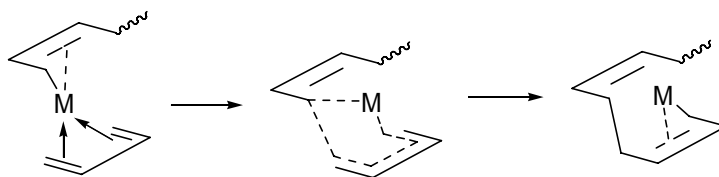


Fig. 4. Possible scheme for the formation of intermediates formed by the last polymerized unit, the cobalt atom and the incoming monomer.

We are currently extending our investigation to the polymerization of various dienes and as well as to various Co(II) catalysts with different ligand structure. In this way we are investigating the influence of the ligand on chemo- and stereoselectivity, confirming the validity of the diene polymerization mechanism previously proposed.

Conclusions

Polymerizations of 1,3-butadiene by a series of prototypical Co(II)-based pyridyl bis(imine) complexes bearing two methyl substituents in different positions on each imine aryl group showed very high polymerization activities associated with ethylaluminum sesquichloride (EAS) as a cocatalyst. The Co(II) catalysts containing less hindered pyridyl bis(imine) ligands showed the highest activity to yield high molecular weight polymers. All catalysts yielded *cis*-1,4-polybutadienes up to 96.4% with *cis*-1,4 regular structure.

Experimental part

General Methods and Materials

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. Polymerization grade of BD (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5 Å/13X. All used reagents were purchased from Aldrich and used without purification. Ethylaluminum sesquichloride was obtained as a 0.9 M total Al solution in toluene. Literature procedures [9] were used to synthesize Co(II)-based pyridyl bis(imine) complexes shown in Fig. 1.

Polymerization procedure

Solution polymerizations of BD were carried out in a high-pressure glass reactor (40 mL) connected with a vacuum system. In a typical procedure, 4 mol of precatalyst ([EAS]/[precatalyst] = 100) was dissolved in 20 mL of toluene. The polymerization started by injecting 1.08 g of 1,3-butadiene (1 mol/L) and EAS into the reactor in this order. The reaction mixture was stirred at 30 °C for 40 min. The resulting solution was poured into acidified methanol (100 mL of a 5 % solution of HCl). The polymer was then isolated by filtration and washed with methanol before drying overnight at 40 °C. Polymer yield was determined by gravimetry.

Polymer analysis

The molecular weights of polybutadiene were determined by gel permeation chromatography (GPC) using a Waters M515 series system in tetrahydrofuran (THF) at 25 °C calibrated with polystyrene standards. The microstructure of polybutadiene was determined by using ¹H NMR and ¹³C NMR spectra recorded on a Varian Unity Plus 300 (300 MHz) spectrometer in CDCl₃ at 25 °C using tetramethylsilane as an internal reference. ¹H NMR: δ = 4.8–5.2 (=CH₂ of 1,2-butadiene unit), 5.2–5.8 (–CH of 1,4-butadiene unit and –CH of 1,2-butadiene unit). ¹³C NMR: δ = 27.4 (1,4-*cis*-butadiene unit), 32.7 (1,4-*trans*-butadiene unit), 127.7–131.8 (1,4-butadiene unit), 113.8–114.8 and 143.3–144.7 (1,2-butadiene unit).

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