

Catalytic Behavior of Co(II) Complexes with 2-(Benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine Ligands on Isoprene Stereospecific Polymerization

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ABSTRACT: Polymerization behaviors of isoprene under different polymerization conditions with 2-(1-methyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl) pyridine cobalt(II) dichloride and ethylaluminum sesquichloride or diethylaluminum chloride catalyst system were evaluated. The effects of temperature, solvents, [Al]/[Co] molar ratio, and the structure of cocatalysts on the catalyst activity and the characteristics of polyisoprenes (PIs) were investigated and optimum conditions for synthesizing stereoselective PIs were obtained. The results showed that pre-catalyst activity was strongly influenced by polymerization temperature, [Al]/[Co] molar ratio and solvents, and the kinds of solvents and cocatalysts affected the microstructures of PIs greatly. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: catalysts; properties and characterization; rubber

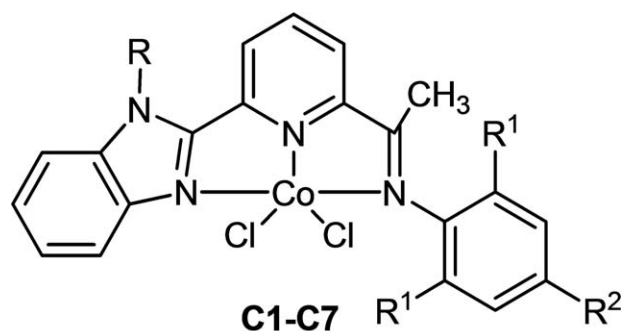
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INTRODUCTION

Great progress has been achieved in polyolefin industry with the development of coordination polymerization catalysts, which played an important role in control of polymer stereoregularities. Among the coordination polymerization catalysts, traditional Ziegler-Natta catalysts^{1–3} with relatively low catalyst cost and easy preparation procedure have been applied widely in the polyolefin industry. Compared with the Ziegler-Natta catalysts featured with multiple active centers, wider molecular weight distribution, and difficulty in reaction with polar monomer, the metallocene catalysts⁴ show higher catalytic activity, single active center, narrower molecular weight distribution, and improved copolymerization behaviors. However, complex synthesis procedures and a large amount of methylaluminoxane (MAO) needed limit the industrial application of the metallocene catalysts. In recent years, the late transition metal complexes catalysts have been of great importance to olefin polymerization in term of scientific research and industrial application. In 1998, Brookhart and coworkers⁵ and Gibson and coworkers⁶ reported the late transition metal catalyst system containing diimine ligands in the presence of MAO for olefin polymerization, respectively. The new generation late transition metal catalyst system showed high catalytic activity and great ability to copolymerization of

olefins with polar monomers. In addition, the late transition metal catalysts are less sensitive catalyst compared to the Ziegler-Natta catalyst and the metallocene catalyst, and can easily realize the control of polymer microstructure and stereoselectivity by regulating the ligands structures. Since 1995, most studies have focused on ethylene oligo-polymerization using late transition metal precatalysts, particularly tridentate cobalt and iron complexes.^{5–15} In the field of diene polymerization, the polybutadienes (PBD) with various stereoregularities (*cis*-1, 4, *trans*-1, 4, 1, 2-*syndiotactic*, 1, 2-*isotactic*, and 1, 2-*atactic*) have been successfully achieved with single-site precatalysts of the lanthanides^{16–33} or the late transition metals.^{34–44} The high *cis*-1, 4-PBD was synthesized by Co(II) precatalysts bearing bis(benzimidazolyl)amine ligands,^{34–36} salen ligands^{37,38} with or without an auxiliary triphenylphosphine (PPh₃). But, there were only several reports involved in stereo-controlled polymerization of isoprene with the cobalt(II) late transition metal catalyst system. Ricci et al. reported that equibinary *cis*-1,4-*alt*-3,4 polyisoprenes were synthesized with the CoCl₂(PPh₂)₂ (R = methyl, ethyl, *n*-propyl, isopropyl, and cyclohexyl)-MAO systems and the mode of formation of the equibinary *cis*-1,4/3,4 polyisoprene was described.^{45–48} To the cobalt(II) catalyst system, polymerization behaviors were complex and affected by different polymerization



	C1	C2	C3	C4	C5	C6	C7
R	Me	Me	Me	Me	Me	Et	i-Pr
R ¹	Me	Me	Et	Et	i-Pr	Me	Me
R ²	H	Me	Me	H	H	H	H

Scheme 1. The structures of a series of cobalt complexes.

conditions and the structures of cocatalysts and precatalysts. No reports were published involved in the systematic evaluation of the polymerization behaviors of isoprene based on the similar cobalt late transition metal catalyst system with a series of polymerization conditions including temperature, [Al]/[Co] molar ratio, solvents and the kinds of cocatalysts.

In this work, the catalyst activity, the characteristics of the obtained polyisoprenes (PIs) were examined carefully under different polymerization conditions with the cobalt(II) catalyst system containing 2-(1-methyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine cobalt(II) dichloride (C2, Scheme 1) as precatalyst and two kinds of low cost cocatalysts other than MAO [ethylaluminum sesquichloride (EASC) and diethylaluminum chloride (DEAC)], which was helpful to understand the polymerization behaviors of the cobalt(II) late transition metal catalyst system in the polymerization of dienes. The correlation between polymerization conditions and the characteristics of PIs with the cobalt late transition metal catalyst system was established for better design and development of new-type PIs materials.

EXPERIMENTAL

Materials

All operations were performed under dry argon by Schlenk techniques, which was quite effective to isolate water and oxygen. Toluene and heptane were deoxygenated by argon purge after refluxed for 48 h and distilled over sodium. Isoprene (Ip) (polymerization grade, Jinshan Petrochemical Company, PetroChina) was distilled over molecular sieve before using. Triethylaluminum (AlEt₃, >98%) was supplied by the Orient Hongye Chemical of China. EASC and DEAC were prepared by the reaction of AlCl₃ and AlEt₃. The cobalt complexes used as precatalysts (Scheme 1) were prepared according to previous procedure.⁴⁹

Polymerization Procedure

The polymerization of isoprene in toluene or heptane was carried out in a Schlenk flask (30 mL). A typical polymerization procedure was as follows: the flask was heated, dried in a vac-

uum, and recharged with nitrogen for three-time cycles by the double manifold. The flask was then filled with nitrogen and the required amount of cobalt complex (precatalyst), toluene or heptane, and isoprene were added into the Schlenk reactor in sequence. Then the cocatalyst EASC or DEAC was injected to initiate the polymerization at different polymerization conditions. After a predetermined reaction time, the polymerization reaction was terminated with a diluted HCl solution of ethanol (100 mL of a 5% v/v solution of HCl). The polymer was collected by filtration and washed with ethanol several times, then dried in a vacuum oven at 40 °C. The conversion was measured by gravimetric method. The obtained weight of polymers (g) divided by the added amount of Co (mol) and polymerization time (h) was catalyst activity.

Measurements

Fourier-transform infrared (FT-IR) spectra were recorded on a Magna-IR Spectrometer 750 instrument using ATR (ZnSe cell) at a resolution of 4 cm⁻¹ by 32 scans. ¹H-NMR (500 MHz) spectra were recorded at 25 °C on a BRUKER 500 MHz spectrometer in CDCl₃ containing tetramethylsilane as a standard. The gel content of PI was obtained through calculating the insoluble weight content of PI in toluene.

According to the calculated area of the characteristic signals at 4.75 and 5.10 ppm, the molar content of 3, 4 PI and *cis*-1, 4 PI based on ¹H-NMR can be calculated, as shown in the following equation:

$$C_{1,4}/C_{3,4} = I(5.10)/(I(4.75)/2)$$

$$C_{1,4} + C_{3,4} = 100$$

Wherein, C_{1,4} and C_{3,4} represent molar percentage of the *cis*-1,4 units and 3, 4 units, respectively; and I(5.10) and I(4.75) represent signal area at 5.10 and 4.75 ppm, respectively.

The microstructures of the PI based on FT-IR spectra can be calculated according to the following equations.^{50–52}

$$A_{1375} = 24 C_{Ip\text{cis-1,4}}L + 32.6 C_{Ip3,4}L$$

$$A_{889} = 101 C_{Ip3,4}L$$

$$Cis-1, 4 PI(\%) = 100 \times C_{Ip\text{cis-1,4}} / (C_{Ip\text{cis-1,4}} + C_{Ip3,4})$$

$$3, 4 PI(\%) = 100 \times C_{Ip3,4} / (C_{Ip\text{cis-1,4}} + C_{Ip3,4})$$

Wherein, A₁₃₇₅ is the absorption intensity at 1375 cm⁻¹, which was expressed by the peak height; C_{Ip*cis*-1,4} represents the molar content of isoprene *cis*-1,4 units, C_{Ip3,4} represents the molar content of isoprene 3, 4 units, L indicates the thickness of the sample.

RESULTS AND DISCUSSION

The behaviors of isoprene polymerization were discussed with 2-(1-methyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine cobalt(II) dichloride (C2, in Scheme 1) as precatalyst based on different [Al]/[Co] molar ratios, solvents, polymerization temperature and the structure of alkyl aluminum. The polymerization results were summarized in Tables I and II. The microstructure of

Table I. Effects of [Al]/[Co] Ratio on Isoprene Polymerization

Run ^a	Precat.	Solvent	Co-cat. ^b	[Al]/[Co] (mol/mol)	Conversion (wt %)	Activity ^c	Gel (wt %)	<i>cis</i> -1,4 ^d (mol %)	3,4 ^d (mol %)	<i>cis</i> -1,4 ^e (mol %)	3,4 ^e (mol %)
a1	C2	Toluene	EASC	200	10.0	0.68	1.1	96.6	3.4	96.5	3.5
a2	C2	Toluene	EASC	300	6.2	0.42	3.1	95.4	4.6	96.9	3.1
a3	C2	Toluene	EASC	400	48.2	3.22	1.2	94.0	6.0	95.9	4.1
a4	C2	Toluene	EASC	500	38.5	2.62	2.7	96.3	3.7	97.1	2.9
a5	C2	<i>n</i> -Heptane	EASC	200	2.6	0.18	39.2	88.5	11.5	86.9	13.1
a6	C2	<i>n</i> -Heptane	EASC	300	1.9	0.13	47.9	90.7	9.3	92.6	7.4
a7	C2	<i>n</i> -Heptane	EASC	400	31.5	2.15	22.6	89.9	10.1	91.2	8.8
a8	C2	<i>n</i> -Heptane	EASC	500	15.5	1.05	24.9	89.7	10.3	89.4	10.6
a9	C2	Toluene	DEAC	200	3.2	0.22	3.8	88.5	11.5	91.8	8.2
a10	C2	Toluene	DEAC	300	3.2	0.22	3.4	90.7	9.3	92.3	7.7
a11	C2	Toluene	DEAC	400	5.0	0.34	3.0	88.9	11.1	90.1	9.9
a12	C2	Toluene	DEAC	500	3.4	0.23	4.7	89.1	10.9	89.5	10.5
a13	C2	<i>n</i> -Heptane	DEAC	200	1.5	0.10	30.2	83.8	16.2	85.2	14.8
a14	C2	<i>n</i> -Heptane	DEAC	300	2.4	0.17	31.5	82.6	17.4	85.1	14.9
a15	C2	<i>n</i> -Heptane	DEAC	400	4.2	0.29	14.2	63.6	36.4	67.9	32.1
a16	C2	<i>n</i> -Heptane	DEAC	500	2.9	0.20	14.6	77.5	22.5	78.2	21.8

^aPolymerization conditions: [Co]/[I_p] = 2×10^{-5} (mol/mol), time = 30 min, temperature = 30 °C; V_{IP} = 8.0 mL, $V_{solvent}$ = 18.7 mL, $M_{[Co]}$ = 1.6×10^{-6} mol.

^bEASC as ethylaluminum sesquichloride and DEAC as diethylaluminum chloride.

^cActivity: 10^6 g PI (mol Co)⁻¹ h⁻¹.

^dDetermined by ¹H-NMR.

^eDetermined by FT-IR.

the PI was measured by ¹H-NMR spectroscopy and shown in Figure 1. The typical NMR chemical shifts and assignments for PI were as follows: δ = 4.7 – 4.8 ppm (=CH₂ of 3, 4-IP unit), δ = 5.0–5.1 ppm (=CH of 1, 4-IP unit).⁴⁵ No resonance signals were observed at δ = 5.9 ppm indicating the absence of 1, 2-units in the PIs. To recognize the *cis-trans* geometric isomers, FT-IR measurements were carried out to characterize the microstructure of the PIs, as shown in Figure 2. The distinct peaks at 1375 cm⁻¹ verified the *cis* nature of the 1,4-units. Weak peaks observed at about 890 cm⁻¹ were assigned to the 3,4 units.^{53,54} Also no existence of *trans*-1, 4 and 1, 2-units has been affirmed by ¹³C-NMR in our previous research.⁵⁵

Effects of [Al]/[Co] Molar Ratio on the Catalytic Behavior of Co Precatalysts

As observed in Table I, the catalyst activity was strongly influenced by the [Al]/[Co] molar ratio. With the increase (from 200, 300, to 400) of the [Al]/[Co] molar ratio, catalyst activity and the conversion of PIs increased. But when the [Al]/[Co] molar ratio exceeded 400, catalyst activity and the conversion of PIs decreased perhaps due to the excess reduction of the active centers. With the increase of [Al]/[Co] ratio, the content of gel and the *cis*-1,4 units kept stable in Table I, which indicated the [Al]/[Co] ratio showed no influence in gel content and the PIs stereoselectivity.

Effects of Polymerization Temperature on the Catalytic Behavior of Co Precatalysts

The effects of polymerization temperature on isoprene polymerization were examined and the results were summarized in Table II. In whole, the conversion of PIs and catalyst activity

first increased with the increase of temperature and reached a peak value, afterwards lowered. For example, at the range of 20–60 °C, the polymerization rate increased with the increase of temperature with EASC as cocatalyst in *n*-heptane. The conversion of PIs could reach 62.5% (b9) for 0.5 h at 60 °C. When the polymerization temperature increased to 70 °C further, catalytic activity reduced instead. The content of *cis*-1,4 units decreased with the increase of polymerization temperature, meanwhile the 3,4-units content increased, even reached 33.9% (b19). The gel content increased with the increase of temperature suggesting that cross-link preferred to occur at higher temperature.

Effects of Different Solvents and Cocatalysts on the Catalytic Behavior of Co Precatalysts

The effects on the catalytic activity, polymer microstructure, and gel content with different solvents were examined and the results were shown in Tables I and II. From Table I (a1 to a8), the Co complexes activated with EASC in toluene exhibited higher activity (from 0.42 to 3.22×10^6 g PI (mol Co)⁻¹ h⁻¹). Instead when using *n*-heptane as solvent, the catalyst activity of the Co catalysts decreased to 0.13 – 2.15×10^6 g PI (mol Co)⁻¹ h⁻¹, which was due to easier stabilization of the active center in toluene than in *n*-heptane. The polymers showed higher content of *cis*-1,4 units (>90%) synthesized in toluene than in *n*-heptane. Further, the types of solvents also had a great influence on gel content. As shown in Table I, the gel content was low (<5%) in toluene, while the obvious increase of

Table II. Effects of Temperature on Isoprene Polymerization

Run ^a	Pre-cat.	Solvent	Co-cat ^b	T (°C)	Conversion (wt %)	Activity ^c	Gel (wt %)	cis-1,4 ^d (mol %)	3,4 ^d (mol %)	cis-1,4 ^e (mol %)	3,4 ^e (mol %)
b1	C2	Toluene	EASC	20	35.1	2.39	0.8			97.3	2.7
b2	C2	Toluene	EASC	30	48.2	3.22	1.2	94.0	6.0	95.9	4.1
b3	C2	Toluene	EASC	50	60.1	4.08	0.6			96.2	3.8
b4	C2	Toluene	EASC	60	36.9	2.51	0.6			95.1	4.9
b5	C2	Toluene	EASC	70	30.2	2.05	1.1			92.1	7.9
b6	C2	<i>n</i> -Heptane	EASC	20	6.3	0.43	30.3			90.8	9.2
b7	C2	<i>n</i> -Heptane	EASC	40	13.1	0.89	33.6			86.9	13.1
b8	C2	<i>n</i> -Heptane	EASC	50	30.6	2.08	43.6			81.3	18.9
b9	C2	<i>n</i> -Heptane	EASC	60	62.5	4.26	47.1			76.4	23.6
b10	C2	<i>n</i> -Heptane	EASC	70	45.2	3.08	59.6			73.2	26.8
b11	C2	Toluene	DEAC	20	6.8	0.46	1.4	96.6	3.4	97.2	2.8
b12	C2	Toluene	DEAC	30	5.0	0.34	3.0	88.9	11.1	90.1	9.9
b13	C2	Toluene	DEAC	50	11.5	0.78	4.1	94.8	5.2	92.0	8.0
b14	C2	Toluene	DEAC	60	1.6	0.11	7.8			92.8	7.2
b15	C2	Toluene	DEAC	70	3.1	0.21	13.2			87.6	12.4
b16	C2	<i>n</i> -Heptane	DEAC	20	2.7	0.18	5.3			82.3	17.7
b17	C2	<i>n</i> -Heptane	DEAC	30	4.2	0.29	14.2	63.6	36.4	67.9	32.1
b18	C2	<i>n</i> -Heptane	DEAC	40	4.9	0.33	4.3			74.1	25.9
b19	C2	<i>n</i> -Heptane	DEAC	50	3.4	0.23	8.3			66.1	33.9
b20	C2	<i>n</i> -Heptane	DEAC	60	1.9	0.13	13.6			75.7	24.3
b21	C2	<i>n</i> -Heptane	DEAC	70	1.6	0.11	25.3			80.4	19.6

^aPolymerization conditions: [Al]/[Co] = 400 (mol/mol), [Co]/[I_p] = 2×10^{-5} (mol/mol), time = 30 min, V_{IP} = 8.0 mL, $V_{solvent}$ = 18.7 mL, $M_{[Co]}$ = 1.6×10^{-6} mol.

^bEASC as ethylaluminum sesquichloride and DEAC as diethylaluminum chloride.

^cActivity: 10^6 g PI (mol Co)⁻¹ h⁻¹.

^dDetermined by ¹H-NMR.

^eDetermined by FT-IR.

gel content was observed (14.2–47.9%) in *n*-heptane, which was perhaps due to the better solubility of isoprene favoring chain propagation during polymerization in toluene than in *n*-heptane. However, the catalytic activity of Co complexes activated

with DEAC decreased towards isoprene polymerization whether in toluene or in *n*-heptane.

The catalytic activity was also influenced by different kinds of alkyl aluminum. As shown in Table I, a3 and a11, the catalyst

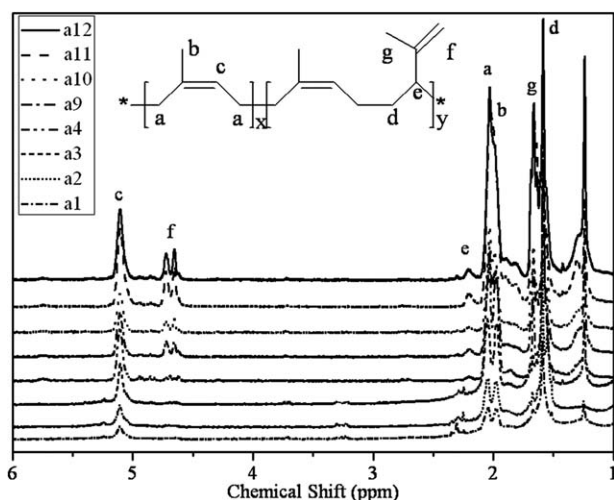


Figure 1. ¹H-NMR spectra of the PIs with Co pre-catalysts.

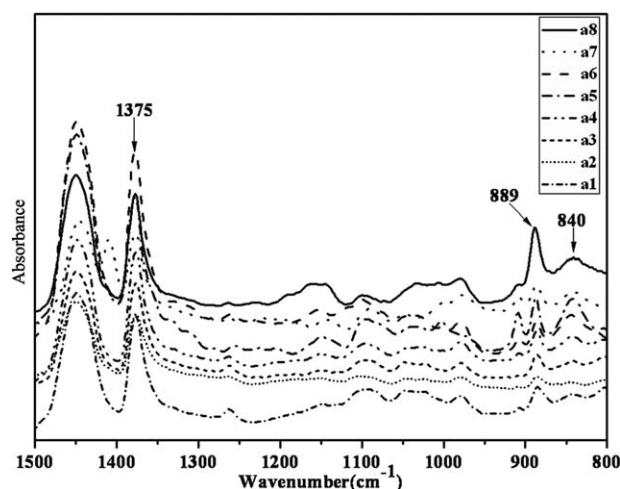


Figure 2. FT-IR spectra of the PIs with Co pre-catalysts.

Table III. Effects of a Series of Precatalysts on Isoprene Polymerization

Run ^a	Pre-cat.	Co-cat. ^b	Conversion (wt %)	Activity ^c	Gel (wt %)	cis-1,4 ^d (mol %)	3,4 ^d (mol %)	cis-1,4 ^e (mol %)	3,4 ^e (mol %)
d1	C1	EASC	89.8	0.77	0.9	96.7	3.3	96.6	3.4
d2	C2	EASC	97.9	0.84	0.4	94.5	5.5	95.5	4.5
d3	C3	EASC	82.6	0.70	29.3	95.7	4.3	94.7	5.3
d4	C4	EASC	50.7	0.43	0.6	93.5	6.5	95.1	4.9
d5	C5	EASC	61.4	0.52	0.2	95.8	4.2	95.3	4.7
d6	C6	EASC	72.8	0.62	14.3	94.9	5.1	95.3	4.7
d7	C7	EASC	94.5	0.80	21.5	95.5	4.5	94.8	5.2

^aPolymerization conditions: [Al]/[Co] = 400 (mol/mol), [Co]/[Ip] = 2×10^{-5} (mol/mol), time = 4 h, temperature = 40 °C, V_{IP} = 8.0 mL, $V_{solvent}$ = 18.7 mL, $M_{[Co]}$ = 1.6×10^{-6} mol.

^bEASC = ethylaluminum sesquichloride.

^cActivity: 10^6 g PI (mol Co)⁻¹ h⁻¹.

^dDetermined by ¹H-NMR.

^eDetermined by FT-IR.

system in combination of EASC showed higher activity [3.22×10^6 g PI (mol Co)⁻¹ h⁻¹ (a3)] than DEAC [0.34×10^6 g PI (mol Co)⁻¹ h⁻¹ (a1)] at 30 °C for 0.5 h with the same [Co]/[Ip] and [Al]/[Co] ratio. The reason was that alkylation reaction of between Co complex and EASC was much easier to occur than that of between Co complex and DEAC, which was beneficial for the formation of the activity center, and finally increased the rate of chain initiation and chain propagation. It was found that the polymers with EASC as cocatalyst contained higher cis-1,4 units (>95%) than those (80–90%) with DEAC as cocatalyst in Table I.

The Discussion of Different Precatalysts

Then a series of experiments in optimized conditions ([Al]/[Co] = 400 (mol/mol), [Co]/[Ip] = 2×10^{-5} (mol/mol), time = 4 h, temperature = 40 °C, toluene as solvent, EASC as cocatalyst) proceeded with a series of Co precatalyst (Scheme 1), and the results were presented in Table III. R₁ groups showed greater influence in polymerization rate than R and R₂ groups, and the catalyst activities decreased with the increase of steric hindrance (R₁). It was found that the Co precatalysts with different ligands showed almost similar stereoregularity of PI containing high cis-1, 4 units (94.7–96.6%), which indicated that modified ligands by alkylation on the phenyl or the benzimidazolyl groups showed almost no influence on polymer microstructure. The PIs with lower gel content (<1%) were obtained with precatalysts (C1, C2, C4, and C5) than those (>10%) with C3, C6, and C7 containing bigger substituent groups.

CONCLUSIONS

The catalyst activities and PI characteristics were evaluated based on different polymerization conditions, which were found that EASC and toluene were favorable for synthesis of PI with high content of cis-1, 4-PI (97.1%) and high catalyst activities [3.22×10^6 g PI (mol Co)⁻¹ h⁻¹]. Then the characteristics of polymerization with a series of Cocontaining complexes with 2-(benzimidazolyl)-6-(1-(arylimino)ethyl) pyridine ligands (catalyst) in optimized conditions were discussed. The Co

precatalysts with small substituent groups were beneficial for the reduction of gel content during polymerization.

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