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Polymerization of 1,3-butadiene catalyzed by Co(II) and Ni(II) complexes of 6,6'-dihydroxy-2,2'-bipyridine ligands: 1,4-*cis*-polymerization versus isospecific 1,2-polymerization†

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Co and Ni complexes having the 6,6'-dihydroxy-2,2'-bipyridine (DHBP) ligand [CoCl₂(dhbp), NiBr₂(dhbp)] in the presence of organoaluminum cocatalysts showed much higher catalytic activity in 1,3-butadiene polymerization than the complexes having the 2,2'-bipyridine or 6,6'-dimethoxy-2,2'-bipyridine ligand without hydroxy groups. The polybutadienes obtained had 1,4-*cis* structure (up to 94.6%). In contrast, addition of 5-norbornene-2-methyl amine in 1,3-butadiene polymerization catalyzed by NiBr₂(dhbp)/methylaluminoxane (MAO) caused a marked change in the microstructure of the polybutadiene to the *iso*-1,2-structure with high chemo- and stereoselectivities (*mm* > 99%).

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Introduction

Polymerization of 1,3-butadiene has long been studied as a process by which the economically favorable monomer is converted into synthetic rubber materials. Many transition metal salts and complexes have been reported to catalyze the polymerization to produce high-mass polymers.^{1–3} Control of the ratio of three possible monomer units, *cis*-1,4-, *trans*-1,4-, and 1,2-butadienyl units, is important, as they affect the properties of poly(butadiene)s. The appropriate choice of the transition metal catalyst and Al or B cocatalyst was reported to regulate the content ratio of the three units significantly. There have been a number of reports on *cis*-1,4-^{4–12} or *trans*-1,4-selective^{13–15} polymerization of butadiene. However, reports on the highly selective 1,2-polymerization of butadiene are less common. Fig. 1 shows selected examples of catalysts for syndio- or isospecific polymerization of 1,3-butadiene. The earliest report on 1,2-selective polymerization is from Natta *et al.* They determined that the use of Cr catalyst

resulted in 1,2-polymerization by X-ray crystallography.^{16,17} More recent studies for the 1,2-polymerization were reported by using Cr,^{18,19} Fe,^{20,21} Co-CS₂,²² and Co-phosphine as catalysts.^{23–25} Most polybutadienes with 1,2-rich structures have a syndiotactic structure, as revealed by NMR studies. Examples of isotactic-1,2-polymerization have been limited to those reported by Natta (the selectivity of which is not clear)¹⁷ and Ricci (1,2-unit = 89.3%, *mm* = 71%).¹⁹

Part of the butadiene polymerization catalysis shows a marked change in regioselectivity depending on the cocatalysts or additives. Nd₃(O^tBu)₉ produces *cis*-1,4-polybutadiene (95%) in the presence of DIBAL-H, whereas *trans*-1,4-

syn-1,2-polybutadiene

Co(acac) ₃ /CS ₂ /AlEt ₃ 1,2 > 99% Ueno <i>et al.</i> ²²	CoCl ₂ (P ⁱ PrPh ₂) ₂ /MAO 1,2 = 89.1%, <i>mm</i> = 63.2% Ricci <i>et al.</i> ²⁴
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Fe(2-ethylhexanoate) ₃ /PO(OPh) ₃ /Al ⁱ Bu ₃ 1,2 = 88.2%, <i>mm</i> = 95.7% Zhang <i>et al.</i> ²⁰

Fe(acac) ₃ /C ₅ H ₃ N{OPO(OPh) ₂ } ₂ -2,6/Al ⁱ Bu ₃ 1,2 = 94.7%, <i>mm</i> = 94.4% Gong <i>et al.</i> ²¹
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iso-1,2-polybutadiene

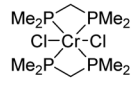
Cr(CNPh) ₆ /AlEt ₃ 1,2 = 97–100% Natta <i>et al.</i> ^{16,17}	 Me ₂ P-CH ₂ -PMe ₂ Cl-Cr-Cl Me ₂ P-CH ₂ -PMe ₂ /MAO 1,2 = 89.3%, <i>mm</i> = 71% Ricci <i>et al.</i> ¹⁹
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Fig. 1 Examples of catalysts for syndio- or isospecific polymerization of 1,3-butadiene.

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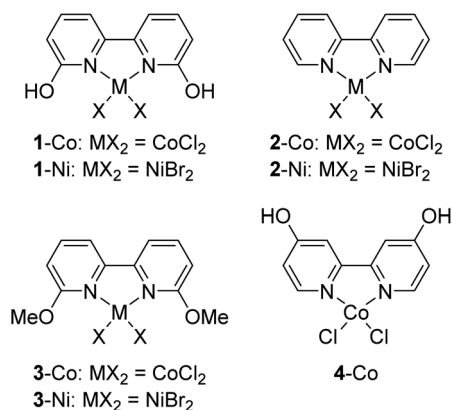
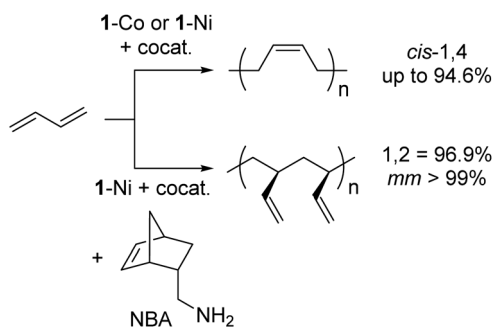


Fig. 2 Ni and Co complexes used in this study.



Scheme 1 Polymerization of 1,3-butadiene by Co and Ni complexes with DHBP ligand.

polybutadiene (95%) forms in the presence of dihexyl magnesium.¹³ CoCl_2 -methylaluminoxane (MAO) affords *cis*-1,4-polybutadiene (>99%) and 1,2-polybutadiene (88%) in the absence and presence of PPh_3 , respectively.⁹ A similar change in the selectivity of *cis*-1,4- and 1,2-polymers is also observed for Co catalysts with tridentate N-ligands.^{11,14,26,27}

Fe and Cu complexes with bipyridine-based ligands have been utilized as catalyst for 1,3-butadiene polymerization.^{28–30} We have also reported that Ni complex with 2,2'-bipyridine ligand brings about *cis*-1,4-selective polymerization of 1,3-butadiene as well as its copolymerization with norbornene.³¹ Herein we report that Co and Ni complexes with the 6,6'-dihydroxy-2,2'-bipyridine (DHBP) ligand (Fig. 2, 1-Co, 1-Ni), which has free hydroxy groups in close proximity to the metal center, show much higher catalytic activity than those without hydroxy groups. In the course of polymerization and copolymerization of butadiene catalyzed by transition metal complexes, we achieved highly isotactic 1,2-polymerization of butadiene by careful choice of the catalyst and additives (Scheme 1).

Results and discussion

1,4-*cis*-polymerization of 1,3-butadiene by Co and Ni complexes with DHBP ligand

Polymerization of 1,3-butadiene in the presence of 1-Co and MAO ($[\text{Co}]/[\text{Al}]/[\text{BD}] = 1/100/5000$) proceeded smoothly at 30 °C

in toluene and produced the polymer with $M_n = 250\,000$ ($M_w/M_n = 2.09$) after 1 h (yield = 87%; run 1 in Table 1). The microstructure was evaluated by IR (Morrello method) to be *cis*-1,4 : *trans*-1,4 : 1,2 = 94.6 : 3.3 : 2.2, indicating a high *cis*-1,4-selectivity of the polymerization.

Other Co complexes, 2-Co, 3-Co, 4-Co, and CoCl_2 produced the polymer in much lower yields under similar conditions (3–8%, runs 2–5). The significant catalytic activity of 1-Co compared with the other Co complexes indicates that the importance of the hydroxy groups of DHBP locating on the position adjacent to the cobalt center.

The lower activity of CoCl_2/MAO than of 1-Co/MAO indicates that the DHBP ligand is not dissociated during the polymerization catalyzed by 1-Co/MAO. 1-Ni also catalyzed the polymerization of 1,3-butadiene smoothly in the presence of the MAO co-catalyst (run 6) to afford a polymer mainly composed of *cis*-1,4-units (*cis*-1,4 = 92.0%, $M_n = 26\,000$). Similarly to the polymerization using the Co complexes, that using 2-Ni and 3-Ni resulted in much lower yields (3 and 12%) (runs 7 and 8).

Isospecific 1,2-polymerization of 1,3-butadiene by Ni complex with DHBP ligand in the presence of 5-norbornene-2-methylamine

Polymerization of 1,3-butadiene using 1-Ni/MAO in the presence of 5-norbornene-2-methylamine (NBA) (mixture of diastereomers, *endo* : *exo* = 83 : 17) ($[\text{NBA}]/[\text{Ni}] = 25$) afforded a polymer in 27% yield (Table 1, run 9).³² In contrast to the *cis*-1,4-selective 1,3-butadiene polymerization using 1-Ni/MAO, the polymer produced was practically insoluble in CHCl_3 and THF. High-temperature SEC of the polymer showed $M_n = 540\,000$ ($M_w/M_n = 2.24$).

The ^1H NMR spectrum of the polymer produced at 100 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ showed major signals of similar intensities attributable to 1,2 units at δ 4.91, 4.89, 5.59, 2.12, 1.14, and 1.35 (Fig. 3(i)).

The COSY spectrum of the polymer indicated that the signals at δ 2.12 and 1.14 are assigned to CH_2 groups on the main chain. Thus, the two hydrogens of the CH_2 groups are not equivalent, which is characteristic of isotactic polymers.^{19,22} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the polymer exhibited signals at δ 113.6, 144.4, 39.0, and 40.7 (Fig. 3(ii) and (iii)). The vinyl CH_2 carbon appeared as a sharp signal at δ 113.6, and no other signals were observed in this area.

This result indicates the very high isotacticity of the polymer (mm > 99%). The NMR spectra also showed the presence of minor signals attributable to *cis*-1,4-butadiene units. The molar ratio of 1,2- to 1,4-units was estimated to be 96.9/3.1 on the basis of ^1H NMR. The ^{13}C NMR chemical shifts of the *cis*-1,4-unit signals agree well with those of the *cis*-1,4-polybutadiene obtained from $\text{NiBr}_2(\text{dhbp})/\text{MAO}$ in the absence of NBA. No signals attributable to the *cis*-1,4-unit connected with a 1,2-unit, which should appear at δ 127.98, 130.05, 24.95, and 32.72, were observed.³³ This result indicates that the polymer produced is a mixture of *cis*-1,4-polybutadiene and *iso*-1,2-polybutadiene. The chemo- and stereoselectivities of *iso*-1,2-polybutadiene are very high.



Table 1 Polymerization of 1,3-Butadiene by Co and Ni catalysts^a

Run	Complex	Additive	Yield ^c %	Activity g mmol M ⁻¹ h ⁻¹	Microstructure ^d (%)			Triad (%)		M _n ^e	M _w /M _n ^e
					<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	rr/rm/mm			
1	1-Co	—	87	232	94.6	3.3	2.2	—		250 000	2.09
2	2-Co	—	8	21	91.2	2.8	6.0	—		330 000	2.08
										12 000	1.26
3	3-Co	—	8	21	94.1	4.2	1.7	—		350 000	1.96
4	4-Co	—	3	7	—	—	—	—		—	—
5	CoCl ₂	—	4	10	97.7	1.0	1.3	—		930 000	1.58
6	1-Ni	—	74	206	92.0	3.9	4.2	—		26 000	2.48
7	2-Ni	—	3	8	92.8	2.7	4.5	—		38 000	1.69
8	3-Ni	—	12	31	90.0	3.2	6.8	—		23 000	1.84
9 ^b	1-Ni	NBA	27	8	3.1	0	96.9	<1/>99		540 000	2.24
10 ^b	1-Ni	NBA-H	87	26	92.5	3.7	3.8	—		14 000	2.45
11 ^b	1-Ni	<i>exo</i> -NBA	17	5	90.1	5.0	4.9	—		6300	3.13
12 ^b	1-Ni	<i>endo</i> -NBA	37	11	20.6	0	79.4	<1/>99		270 000	3.69
										7700	1.64
13 ^b	2-Ni	NBA	5	1	90.8	2.4	6.8	—		15 000	2.08
14 ^b	1-Co	NBA	35	10	91.4	5.8	2.8	—		35 000	2.41

^a [BD]/[Co or Ni]/[Al] = 5000/1/100, [catalyst] = 0.02 mmol, toluene = 30 mL, 30 °C, 1 h. ^b [BD]/[catalyst]/[Al]/[additive] = 500/1/100/25. ^c Methanol-insoluble part. ^d Determined by FT-IR or NMR (C₂D₂Cl₄, 100 °C). ^e Determined by SEC.

The polymerization by 1-Ni/MAO in the presence of 2-norbornylmethylamine (NBA-H) without a C=C double bond produced *cis*-1,4-polybutadiene with *M_n* = 14 000 (Table 1, run 10). 2-(1-Cyclohexenyl)ethylamine or methallylamine with both alkenyl and amino groups did not produce polymer. The polymerization in the presence of *exo*-NBA resulted in a polymer with the *cis*-1,4 structure (*cis*-1,4 = 90.1%), whereas that in the presence of *endo*-NBA afforded a polymer mainly with highly

isotactic 1,2-polybutadiene (*mm* > 99%). A bimodal molecular weight distribution of the polymer produced indicates that the product is a mixture of *cis*-1,4-polybutadiene and *iso*-1,2-polybutadiene, as noted above. These results suggest that an appropriate position of the C=C double bond and amino group in *endo*-NBA is essential for the formation of *iso*-1,2-polybutadiene.

Although 1-Ni/MAO/NBA is effective for the *iso*-1,2-polymerization of 1,3-butadiene, 2-Ni/MAO/NBA formed an oily polymer rich in *cis*-1,4 units (*cis*-1,4 = 90.8%; run 13). 1-Co/MAO also catalyzed the polymerization in the presence of NBA to yield an oily product having mainly *cis*-1,4-units (91.4%; run 14). Thus, the DHBP ligand is also necessary for the *iso*-1,2-polymerization of 1,3-butadiene.

To obtain further details on the effect of NBA, polymerization by 1-Ni/MAO/NBA was conducted using various molar ratios of [Ni]/[Al]/[NBA] (Table S1†). The catalyst with [Ni]/[Al]/[NBA] = 1/100/9 yielded a polybutadiene with *cis*-1,4- and 1,2- forms in 91.8/3.9 ratio (92% yield). Changing the [Ni]/[NBA] molar ratio to 1/18 and then to 1/33 resulted in an increase in the amount of 1,2-units to 25 and 91.3%, respectively. A further increase in the amount of NBA resulted in no polymerization products. The amount of Al also affects the yield and structure of the polymer. The catalyst with [Ni]/[Al]/[NBA] = 1/50/25 did not produce the polymer. On the other hand, in the reaction using [Al]/[Ni] = 150, polybutadiene containing 34% 1,2-units was obtained in 64% yield. In the case of [NBA]/[Ni] = 200, the amount of the 1,2-unit decreased to 7.6% with an increase in the total yield to 82%.

DSC analysis of *iso*-1,2-polybutadiene (Table 1, run 9) showed its melting point to be 122.5 °C (Fig. S9†). XRD measurement of *iso*-1,2-polybutadiene showed four sharp diffractions (at 3.51, 4.32, 5.01, and 8.70 Å) on an amorphous

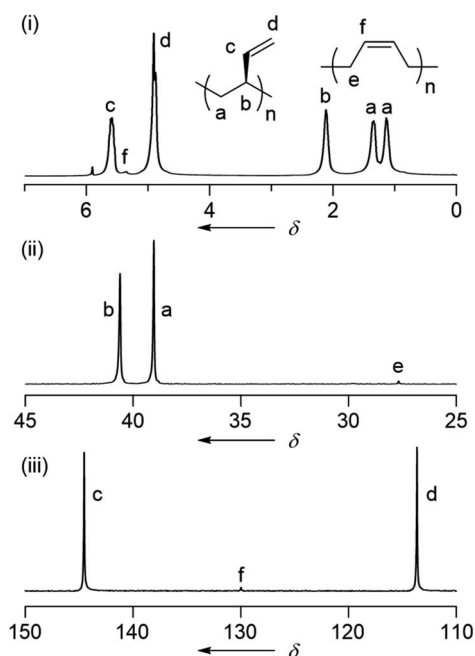


Fig. 3 (i) ¹H and (ii and iii) ¹³C NMR spectra (C₂D₂Cl₄, 100 °C) of polybutadiene obtained from 1-Ni/MAO/NBA (run 9, Table 1).



part produced by *iso*-1,2-polybutadiene (Fig. S10†); these results are consistent with those reported by Natta. The crystallinity of this sample was calculated to be 57%, which is higher than the crystallinity of *iso*-1,2-polybutadiene reported by Natta (45%).

Polymerization mechanism

On the basis of the above results, the mechanism of 1,3-butadiene polymerization by the Co and Ni catalysts with DHBP may be described as follows. The OH groups of the DHBP ligand strongly interact with the Al-containing cocatalyst. The higher catalytic activity of 1-Co than that of 4-Co suggests that the Al moiety positioned close to the metal center plays an essential role in enhancing the reaction. 1,3-Butadiene undergoes *s-cis*- η^4 coordination to the metal center and is inserted into the metal–polymer bond to form an anti- π -allylic polymer end attached to the metal center. Further insertion of 1,3-butadiene leads to the formation of *cis*-1,4-polybutadiene. The higher catalytic activity of the complex with the DHBP ligand can be due to the interaction between the Al center located close to the metal center and the unsaturated group of the growing chain end. The possible mechanisms involve the formation of a σ -allyl–metal intermediate induced by the aggregation of the Al cocatalyst (Fig. 4(i)) and coordination of an inner olefin unit in the polybutadiene chain to the Al center (Fig. 4(ii)).

Addition of NBA to the 1-Ni/MAO catalyst markedly changes the chemo- and stereoselectivities from *cis*-1,4 to *iso*-1,2. The high 1,2-selectivity of the polymerization can be ascribed to 1,2-insertion rather than 2,1-insertion of 1,3-butadiene to the polymer chain end. A possible mechanism of the formation of *iso*-1,2-polybutadiene involves the interaction of the amino group and C=C bond of NBA with the Al center on the hydroxy group of the ligand and the Ni center, respectively (Fig. 4(iii)). The olefin group of the NBA unit may act as a hemilabile ligand and allow coordination of 1,3-butadiene to the Ni center, and 1,2-insertion of 1,3-butadiene owing to its steric bulkiness. The chiral structure of NBA renders the stereoselective insertion of 1,3-butadiene, realizing a highly isotactic structure of the produced polymer.

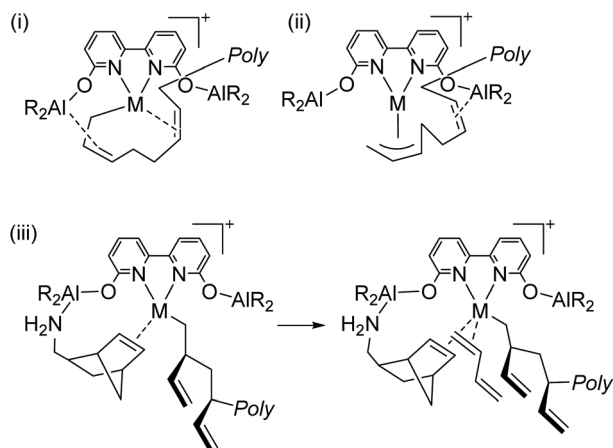


Fig. 4 Possible intermediate in the polymerization of 1,3-butadiene by 1-Co, 1-Ni/MAO ((i) and/or (ii)) and 1-Ni/MAO/NBA (iii).

When the NBA-to-Al ratio is low (0.09 to 0.125, Table S1,† runs 1 and 8), most of the NBA molecules would interact with MAO rather than with the Ni complex, which prevents the formation of 1,2-selective active species and results in *cis*-1,4-selective polymerization. When the NBA-to-Al ratio is increased to 0.167 to 0.33 (Table S1,† runs 2, 3, 7, and 9), more amount of 1,2-selective active species generates. However, the NBA-to-Al ratio is further increased to over 0.4, some NBA molecules would interact directly with the Ni center and disturb the interaction of 1,3-butadiene with the catalyst (Table S1,† runs 4–6).

In summary, Co and Ni complexes having a DHBP ligand show higher activity than Co complexes having other bipyridine ligands and produce polybutadiene with the *cis*-1,4-structure. In contrast, the polymerization using 1-Ni/MAO in the presence of an NBA additive afforded a polymer having the *iso*-1,2-structure (*mm* > 99%). The DHBP ligand and *endo*-NBA unit are essential for the formation of *iso*-1,2 polybutadiene.

Experimental

General

All manipulations of the reactions were carried out under nitrogen or argon using standard Schlenk techniques. NMR (^1H and $^{13}\text{C}\{^1\text{H}\}$) spectra were recorded on a Bruker biospin-AVANCE III (400 MHz), biospin-AVANCE III HD (500 MHz) or JEOL-ECA400 spectrometer. The peaks were referenced to CHCl_3 (δ 7.26) in the CDCl_3 solvent, 1,1,2,2-tetrachloroethane (δ 5.91) in the 1,1,2,2-tetrachloroethane- d_2 solvent, for ^1H and CDCl_3 (δ 77.0), and 1,1,2,2-tetrachloroethane- d_2 (δ 74.2) for ^{13}C . IR was recorded on a JASCO FT/IR-4100 equipped with an ATR PRO450-S. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV-vis detector, using THF as eluent at a flow rate of 0.6 mL min^{-1} with TSKgel SuperHM-L and TSKgel SuperHM-M columns. In the case of high temperature GPC analysis, measurement was at 140 °C on a TOSOH HL-8321GPC/HT with a differential refractometer detector, using 1,2,4-trichlorobenzene as eluent. DSC was recorded on SeikoDSC6200R instruments. XRD was recorded on Rigaku NANO-Viewer. Elemental analysis was carried out with a J-Science MICRO CORDER JM10.

Toluene was deoxygenated and dried by using the solvent purification system of a Glass Contour Co. 1,3-Butadiene was dehydrated and deoxygenated by passing through columns GC-RX and DC-A4 (Nikka Seiko Co., Ltd). 5-Norbornene-2-methylamine (NBA) was purchased from TCI or Enamine Ltd and was dehydrogenated by molecular sieve 3A and purified by distillation. CDCl_3 were dehydrogenated by CaH_2 and purified by distillation. Methylaluminoxane (MAO) was purchased from Tosoh Chemical Co. 2-Co,³⁴ 2-Ni,³⁵ 6,6'-dimethoxy-2,2'-bipyridine,³⁶ 4,4'-dihydroxy-2,2'-bipyridine,³⁷ 2-norbornylmethylamine (NBA-H),³⁸ *endo*- or *exo*-5-norbornene-2-methylamine(*endo*- or *exo*-NBA) were prepared according to the literature.^{39–41} CoCl_2 , NiBr_2 , MeOH, EtOH, BHT (2,6-di-*tert*-butyl-



p-methylphenol), and HCl aq. were used as purchased. Dehydrated THF was purchased from Kanto Chemical Co.

Synthesis of Co and Ni complexes

DHBP (94 mg, 0.50 mmol) and CoCl_2 (65 mg, 0.50 mmol) were dissolved in THF (5 mL) in a Schlenk flask, and the mixture was refluxed for 12 h. The green precipitate, thus formed, was filtered and washed with 10 mL of Et_2O twice and dried under a vacuum to give 158 mg (98% yield) of 1-Co as green solid. IR(ATR): 3202, 1600, 1582, 1480, 1434, 1359, 1311, 1278, 1257, 1135, 1013, 981, 799 cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{CoN}_2\text{O}_2$: C, 37.77; H, 2.54; N, 8.81, found: C, 37.76; H, 2.57; N, 8.68. 3-Co and 4-Co were synthesized in a similar manner using 6,6'-dimethoxy-2,2'-bipyridine and 4,4'-dihydroxy-2,2'-bipyridine, respectively. 3-Co: green solid. 71% yield. IR(ATR): 3073, 2980, 2866, 1599, 1572, 1480, 1424, 1342, 1296, 1268, 1147, 1078, 1034, 1011, 795 cm^{-1} . Anal. calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{CoN}_2\text{O}_2$: C, 41.65; H, 3.50; N, 8.09, found: C, 41.41; H, 3.35; N, 8.11. 4-Co: Skyblue solid. 98% yield. IR(ATR): 3280, 3207, 1608, 1582, 1498, 1446, 1369, 1317, 1263, 1218, 1017, 970, 871, 846 cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{CoN}_2\text{O}_2$: C, 37.77; H, 2.54; N, 8.81, found: C, 37.84; H, 2.91; N, 8.62. 1-Ni and 3-Ni were synthesized in a similar manner using $\text{NiBr}_2(\text{dme})$. 1-Ni: yellowish brown solid. 85% yield. IR(ATR): 3245, 1601, 1581, 1484, 1440, 1355, 1335, 1304, 1279, 1247, 1138, 1017, 972, 799 cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_8\text{Br}_2\text{N}_2\text{NiO}_2$: C, 29.53; H, 1.98; N, 6.89, found: C, 29.13; H, 1.92; N, 6.75. 3-Ni: pink solid. 92% yield. IR(ATR): 3090, 2981, 2865, 1596, 1571, 1478, 1424, 1340, 1296, 1267, 1147, 1080, 1034, 797 cm^{-1} . Anal. calcd for $\text{C}_{12}\text{H}_{12}\text{Br}_2\text{N}_2\text{NiO}_2$: C, 33.15; H, 2.78; N, 6.44, found: C, 32.91; H, 2.85; N, 6.44.

Polymerization of 1,3-butadiene

To a 200-mL, thick-wall glass bottle containing a 1-Ni (8.1 mg, 0.020 mmol), toluene (9.3 mL) was added under Ar. 1,3-Butadiene (540 mg, 10.0 mmol) was introduced at -20°C . A toluene solution of MAO (2.89 M in toluene, 0.70 mL, 2.0 mmol) was added, and the mixture was warmed to 30°C . As for the *cis*-1,2-polymerization of 1,3-butadiene, NBA (63 mg, 0.50 mmol) was added before the addition of MAO. After 1 h, the reaction was quenched by adding a small portion of EtOH, and the reaction mixture was poured into a solution of HCl (5%) in MeOH containing 100 mg of BHT. The white precipitate was filtered and dried *in vacuo*. Yields were calculated based on the weight of isolated polybutadiene divided by the weight of introduced 1,3-butadiene (540 mg).

Evaluation of microstructure of polybutadiene

Ratio of the microstructure of the butadiene units in the polymer was calculated from the IR peak area ratio using the following equation (Morero method).⁴²

$$C = 1.7455 \times (\log(T_{\text{BL}}/T_{\text{cis}})) - 0.0151 \times (\log(T_{\text{BL}}/T_{\text{vinyl}}))$$

$$T = 0.4292 \times (\log(T_{\text{BL}}/T_{\text{trans}})) - 0.0129 \times (\log(T_{\text{BL}}/T_{\text{vinyl}})) - 0.0454 \times (\log(T_{\text{BL}}/T_{\text{cis}}))$$

$$V = 0.3746 \times (\log(T_{\text{BL}}/T_{\text{vinyl}})) - 0.007 \times (\log(T_{\text{BL}}/T_{\text{cis}}))$$

$$\text{Cis}\% = C/(C + T + V) \times 100$$

$$\text{Trans}\% = 100 - \text{cis}\% - \text{vinyl}\%$$

$$\text{Vinyl}\% = V/(C + T + V) \times 100$$

The peaks and their positions are as follows:

$$T_{\text{cis}}: 735 \text{ cm}^{-1}, T_{\text{vinyl}}: 911 \text{ cm}^{-1}, T_{\text{trans}}: 968 \text{ cm}^{-1}, T_{\text{BL}}: 1130 \text{ cm}^{-1}$$

Ratio of the microstructure of the butadiene units in the *iso*-1,2-polybutadiene was calculated from the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR peak area ratio using the following eq.

$$[1,2\text{-unit}]/([1,2\text{-unit}] + [1,4\text{-unit}]) = V^1/(V^1/2 + C^2, T^2 + V^2)$$

$$[cis\text{-}1,4\text{-unit}]/([cis\text{-}1,4\text{-unit}] + [trans\text{-}1,4\text{-unit}]) = (C^1 + C^{1'} + C^{1''})/[(C^1 + C^{1'} + C^{1''}) + (T^1)]$$

The signals and their positions are as follows: ^1H NMR: δ 4.71–5.12 (V^1), 5.27–5.47 (C^2 , T^2), and 5.47–5.80 (V^2). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 25.2 ($C^{1''}$), 27.7 (C^1), 32.8 (T^1), 32.9 ($C^{1'}$).

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no conflicts of interest.

Notes and references

- G. Ricci, A. Sommazzi, F. Masi, M. Ricci, A. Boglia and G. Leone, *Coord. Chem. Rev.*, 2010, **254**, 661–676.
- Z. Zhang, D. Cui, B. Wang, B. Liu and Y. Yang, *Struct. Bonding*, 2010, **137**, 49–108.
- G. Ricci and G. Leone, *Polyolefins J.*, 2014, **1**, 43–60.
- L. Annunziata, S. Pragliola, D. Pappalardo, C. Tedesco and C. Pellecchia, *Macromolecules*, 2011, **44**, 1934–1941.
- S. Kaita, Z. Hou and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 9078–9079.
- S. Kaita, Y. Takeguchi, Z. Hou, M. Nishiura, Y. Doi and Y. Wakatsuki, *Macromolecules*, 2003, **36**, 7923–7926.
- Y. Guangqian, L. Yuliang, Q. Yahuan and L. Xiaoli, *Macromolecules*, 1993, **26**, 6702–6705.
- S. Kaita, M. Yamanaka, A. C. Horiuchi and Y. Wakatsuki, *Macromolecules*, 2006, **39**, 1359–1363.
- D. C. D. Nath, T. Shiono and T. Ikeda, *Macromol. Chem. Phys.*, 2003, **204**, 2017–2022.



- 10 H. Liu, X. Jia, F. Wang, Q. Dai, B. Wang, J. Bi, C. Zhang, L. Zhao, C. Bai, Y. Hu and X. Zhang, *Dalton Trans.*, 2013, **42**, 13723–13732.
- 11 B. Dong, H. Liu, C. Peng, W. Zhao, W. Zheng, C. Zhang, J. Bi, Y. Hu and X. Zhang, *Eur. Polym. J.*, 2018, **108**, 116–123.
- 12 H. Sato and Y. Yagi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1299–1306.
- 13 J. Gromada, L. le Pichon, A. Mortreux, F. Leising and J.-F. Carpentier, *J. Organomet. Chem.*, 2003, **683**, 44–55.
- 14 R. Cariou, J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov and M. R. J. Elsegood, *Macromolecules*, 2009, **42**, 1443–1444.
- 15 Q. Dai, X. Zhang, Y. Hu, J. He, C. Shi, Y. Li and C. Bai, *Macromolecules*, 2017, **50**, 7887–7894.
- 16 G. Natta and P. Corradini, *J. Polym. Sci.*, 1956, **20**, 251–266.
- 17 G. Natta, L. Porri, G. Zanini and A. Palvarini, *Chim. Ind.*, 1959, 1163.
- 18 G. Ricci, M. Battistella and L. Porri, *Macromolecules*, 2001, **34**, 5766–5769.
- 19 G. Ricci, A. Forni, A. Boglia and M. Sonzogni, *Organometallics*, 2004, **23**, 3727–3732.
- 20 W. Pan, H. Chen, R. Sun, D. Gong, X. Jia, Y. Hu and X. Zhang, *Ind. Eng. Chem. Res.*, 2016, **55**, 7580–7586.
- 21 D. Gong, W. Pan, T. Zhu, H. Chen, Z. Zhou, F. Jiang, Y. Hu and X. Zhang, *Polymer*, 2016, **98**, 136–142.
- 22 H. Ashitaka, K. Inaishi and H. Ueno, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 1973–1988.
- 23 Z. Cai, M. Shinzawa, Y. Nakayama and T. Shiono, *Macromolecules*, 2009, **42**, 7642–7643.
- 24 G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti and F. Bertini, *Macromolecules*, 2005, **38**, 1064–1070.
- 25 Y. Jang, P. Kim and H. Lee, *Macromolecules*, 2002, **35**, 1477–1480.
- 26 R. Cariou, J. J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov, G. J. P. Britovsek and A. J. P. White, *Dalton Trans.*, 2010, **39**, 9039–9045.
- 27 D. Gong, X. Zhang and K.-W. Huang, *Dalton Trans.*, 2016, **45**, 19399–19407.
- 28 C. Bazzini, A. Giarrusso and L. Porri, *Macromol. Rapid Commun.*, 2002, **23**, 922–927.
- 29 G. Ricci, D. Morganti, A. Sommazzi, R. Santi and F. Masi, *J. Mol. Catal. A: Chem.*, 2003, **204–205**, 287–293.
- 30 G. Ricci, G. Leone, G. Zanchin, F. Masi, M. Guelfi and G. Pampaloni, *Molecules*, 2023, **28**, 374.
- 31 S. Yamakawa, D. Takeuchi, K. Osakada, S. Takano and S. Kaita, *React. Funct. Polym.*, 2019, **136**, 19–24.
- 32 We have conducted the 1,3-butadiene polymerization under the same reaction conditions as Table 1, run 9, using NBA purchased from a different supplier (Enamine Co. Ltd) (Table 1, run 9: NBA purchased from TCI). In this case, we obtained polybutadiene in similar yield (26%). Although the 1,2-selectivity (93.5%) was lower than that in Table 1, run 9, we could confirm the reproducibility of the highly 1,2-selective polymerization under the reaction conditions (Table S1, run 9).
- 33 N. Makhyanov, M. M. Minnegaliev and R. M. Aminova, *Polym. Sci., Ser. A*, 2016, **58**, 121–129.
- 34 M. N. Khrizanforov, S. O. Strekalova, T. V. Gryaznova, V. V. Khrizanforova and Y. H. Budnikova, *Russ. Chem. Bull.*, 2015, **64**, 1926–1932.
- 35 M. Bialek, H. Cramail, A. Deffieux and S. M. Guillaume, *Eur. Polym. J.*, 2005, **41**, 2678–2684.
- 36 X. J. Dai and C. J. Li, *J. Am. Chem. Soc.*, 2016, **138**, 5433–5440.
- 37 Y.-R. Hong and C. B. Gorman, *J. Org. Chem.*, 2003, **68**, 9019–9025.
- 38 Y. V. Popov, V. M. Mokhov and D. N. Nebykov, *Russ. J. Gen. Chem.*, 2014, **84**, 444–448.
- 39 J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, 1959, **81**, 4083–4087.
- 40 J. K. Pontrello, M. J. Allen, E. S. Underbakke and L. L. Kiessling, *J. Am. Chem. Soc.*, 2005, **127**, 14536–14537.
- 41 E. M. Kolonko, J. K. Pontrello, S. L. Mangold and L. L. Kiessling, *J. Am. Chem. Soc.*, 2009, **131**, 7327–7333.
- 42 D. Morero, A. Santambrogio, L. Porri and F. Ciampelli, *Chem. Ind.*, 1959, **41**, 758–762.

