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Synthesis of low to high molecular weight poly(1-hexene); rigid/flexible structures in a di- and mononuclear Ni-based catalyst series†

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1-Hexene was polymerized with mono- (MC_n, n = 1–3) and dinuclear (BC_n, n = 1–7) α-diimine Ni-based catalysts bearing different backbones, *ortho*-substituents and spacers between the active centers. Significantly, catalyst BC_2 through an optimum bulkiness in its structure and electronic and steric effects, had the highest activity among all the dinuclear and mononuclear analogues, and made poly(1-hexene) with high M_w (1.7×10^6 g mol^{-1}) and a narrow MWD (2.2). Moreover, a lower level of branching density was observed for the samples obtained by catalysts BC_1 and BC_2 (83–85/1000C) in comparison to MC_{1-3} (107–120/1000C) and BC_{3-7} (131–150/1000C).

The properties of polyolefins in particular can be dramatically tuned by the type of catalyst used in the polymerization.[1,2] Among these polyolefins, poly(1-hexene) or poly(1-octene) have several applications as lubricants, adhesives, linings, elastomers, and drag-reducing agents.[3] The microstructures of these polymers can be controlled by changing the catalyst structure and polymerization conditions. The ability of late transition metal catalysts to yield branched polyolefins without using comonomers, be activated with different cocatalysts, and synthesize functional copolymers has been considered their main advantages.[4] Moreover, the backbone structure, spacer nature, and substituent positions of these catalysts determine their behaviour and the properties of the produced polymers. Besides, cooperative effects in multinuclear catalysts can affect the polymer architecture.[1] Cooperative effects are expressed when secondary interactions take place between weakly basic monomer substituents (such as C–H or –Ph structures) and a second metal center. The steric and electronic effects of the bulky groups surrounding the metal center, along with the nuclearity effect in terms of synergistic reactivity patterns involving two or more metal centers, affect propagation, chain transfer, and chain walking rates, and consequently the molecular weight and branching frequency of the produced polymers. These phenomena depend strongly on the catalyst architecture, and in dinuclear complexes on interactions between the active centers.

Although the background of this work is consistent with our and other previous reports on different types of substituents, bridges and backbones in late transition metal catalysts based on Ni which were used in the (co)polymerization of ethylene and a broad distribution of products is reported, the effect of length, nature and groups on the bridge structure is still an ambiguous point regarding the previous results.[5–12,14] In addition, there should be an optimum electronic environment for active sites to show efficient synergistic and cooperative effects. It could be concluded that the structural features such as the absence or non-effective protection of axial sites can make the catalyst an oligomer producer or a producer of mixtures of oligomers, waxes and low to high molecular weight polymers. Moreover, the length and nature (rigid/flexible) of the bridge in regard to cooperative effects are very crucial, where a long distance between the active sites can cause an independent behavior of each center. This behavior can also be observed if bulky substituents are replaced on the *ortho* position of the aromatic rings in the bridge structure. In contrast, the performance of the metal centers in close proximity is different. As the nature and length of the bridge are important, the presence of substituents also has a high impact on the behavior of the catalysts. Besides, the effect of monomer length could be remarkable as well as an agostic interaction between the atom of the pendant groups and the second metal center.

Herein, we investigated how different backbones, substituents, and linkage structures affect the behaviour of α-diimine Ni-based catalysts at various [Al]/[Ni] molar ratios for the production of poly(1-hexene). Organic ligands and complex structures bearing acenaphthene and methyl groups on the backbone, methyl and isopropyl groups on the aryl rings, and rigid/flexible bridges with different distances between the metal centers were studied.

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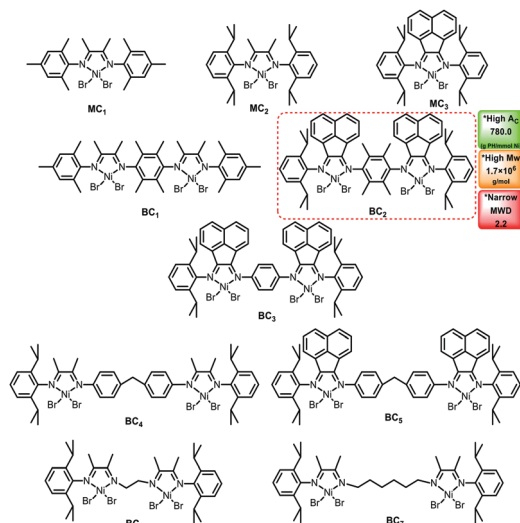
Fig. 1 Synthesized structure of the complexes MC$_n$, n = 1–3 and BC$_n$, n = 1–7.

Fig. 2 Productivities and molecular weights of entries 3, 5 and 10.

These features had a significant effect on the activity, stability, and cooperative effect of the catalyst, and influenced the molecular weight and polydispersity index of the produced poly(1-hexene).

Three mononuclear (MC$_n$, n = 1–3) and seven dinuclear (BC$_n$, n = 1–7) complexes (see Fig. 1) were used to polymerize 1-hexene in the presence of different concentrations of diethyl-aluminium chloride (DEAC). The activity of virtually all complexes had an optimum [Al]/[Ni] molar ratio, after which catalyst activity decreased. This behavior can be explained by considering that a certain [Al]/[Ni] ratio is needed to activate all metal centers, but above this optimal value, the active center concentration will drop due to the formation of cocatalyst-deactivated species.[13,14] Some of our dinuclear catalysts had higher activities than the mononuclear analogues, likely because of the optimum bulkiness and synergistic effect between the two sites.[5,6,14]

The mononuclear complexes had moderate activities in the order MC$_3$ > MC$_2$ > MC$_1$ (Table 1 and Fig. 2). It has been shown that bulky groups such as acenaphthene in the backbone structure (steric effect) can block equatorial sites on the metal center and open axial sites, increasing the catalyst activity.[14–21] In contrast, the observed lower molecular weight for poly(1-hexene)

is due to the electronic effect of the acenaphtyl groups which increases the electron deficiency on the site and chain transfer reactions.[14,17–19] These trends were observed from MC$_2$ to MC$_3$ and from BC$_4$ to BC$_5$ (Tables 1, 2 and Fig. 2 and 3). It should be noted that when isopropyl groups are substituted with methyl or hydrogen, the "ortho-aryl effect" is observed.[7,14,17,20–23] This effect increases polymer M_v, M_w and catalyst activity. Based on this, MC$_2$ showed greater activity than MC$_1$, and BC$_2$ higher than BC$_3$. These results were also confirmed by the presence of the less withdrawing groups (hydrogen atoms) on the *para* position.[24]

For the dinuclear catalysts, the same behavior; BC$_2$ > BC$_5$ > BC$_4$ > BC$_3$ > BC$_1$ > BC$_7$ > BC$_6$ was observed regarding the structure effect (Table 2 and Fig. 2). The higher productivity of BC$_2$ than the other mono and dinuclear catalysts can also be attributed to the optimum bulkiness around the active site which promotes the synergistic effect of the ligand structure (bridge, backbone and substituents).[5,14] In the comparison of the dinuclear and mononuclear analogues, the catalyst productivities

Table 1 1-Hexene polymerization using MC$_n$, n = 1–3 catalysts

Entry	Cat.	[Al]/[Ni]	Yield (g)	Con. (%)	Activity (g PH per mmol Ni)	M_v 10^5 (g/mol)
1	MC$_1$	500	0.69	10.2	233.0	3.9
2	MC$_1$	1000	0.83	12.3	276.7	3.5
3	MC$_1$	1500	0.43	6.4	143.3	4.4
4	MC$_1$	2500	0.20	3.0	66.7	2.1
5	MC$_2$	500	0.93	13.8	309.0	10.6
6	MC$_2$	1000	1.20	17.8	401.0	9.3
7	MC$_2$	1500	1.00	14.9	333.0	5.9
8	MC$_3$	500	1.92	28.5	640.0	2.9
9	MC$_3$	1000	2.20	32.7	733.3	3.5
10	MC$_3$	1500	2.01	29.9	670.0	4.4

Polymerization conditions: DEAC as the cocatalyst, [catalyst] = 3 × 10^{-3} mmol, room temperature, polymerization time = 24 h, 10 cc toluene as the solvent.

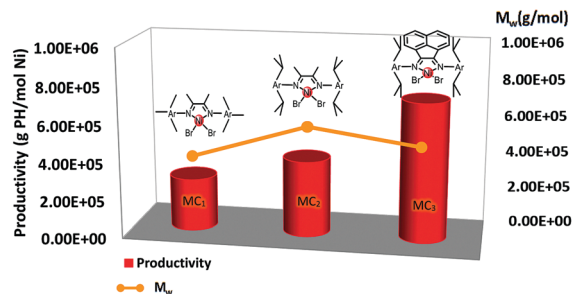**Table 2** 1-Hexene polymerization using BC$_n$, n = 1–7 catalysts

Entry	Cat.	[Al]/[Ni]	Yield (g)	Con. (%)	Activity (g PH per mmol Ni)	M_v 10^5 (g mol^{-1})
11	BC$_1$	500	0.62	9.2	206.8	3.8
12	BC$_1$	1000	0.83	12.3	276.7	3.5
13	BC$_1$	1500	1.23	18.3	410.0	5.6
14	BC$_1$	2500	0.41	6.1	136.7	2.6
15	BC$_2$	1000	1.12	16.6	373.3	11.3
16	BC$_2$	1500	2.34	34.8	780.0	14.7
17	BC$_2$	2000	2.2	32.7	733.3	12.8
18	BC$_2$	2500	1.91	28.4	636.6	7.9
19	BC$_3$	1500	0.70	10.4	233.3	0.9
20	BC$_3$	2000	1.43	21.2	476.6	1.4
21	BC$_3$	2500	0.93	13.8	310.0	2.1
22	BC$_4$	1500	1.14	16.9	380.0	1.6
23	BC$_4$	2500	1.36	20.2	453.3	1.1
24	BC$_4$	3000	1.45	21.5	483.3	0.8
25	BC$_5$	1500	1.04	15.4	346.6	3.4
26	BC$_5$	2000	1.49	22.1	496.6	1.7
27	BC$_5$	2500	1.74	25.9	580.0	2.3
28	BC$_5$	3000	1.52	22.6	506.6	0.6
29	BC$_6$	1000	1.12	16.6	373.3	1.1
30	BC$_6$	1500	1.07	15.9	356.6	4.5
31	BC$_6$	2000	0.84	12.5	280.0	0.7
32	BC$_7$	1000	0.81	12.0	270.0	5.1
33	BC$_7$	1500	1.16	17.2	386.7	3.4
34	BC$_7$	2000	1.06	15.8	353.3	0.6

Polymerization conditions: DEAC as the cocatalyst, [catalyst] = 3 × 10^{-3} mmol, room temperature, polymerization time = 24 h, 10 cc toluene as the solvent.
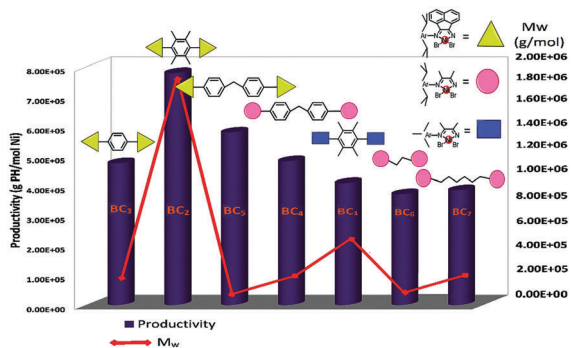
Fig. 3 Productivities and molecular weights of entries 13, 16, 21, 22, 25, 29 and 31.

Table 3 GPC results of the poly(1-hexene) samples produced using the mononuclear and dinuclear catalysts[a]

Entry[b]	Cat.	M_n	M_w	MWD	CH_3 (/1000C)
3	MC_1	184 530	387 510	2.1	119.6
5	MC_1	257 300	514 580	2.0	117.3
10	MC_1	232 860	419 140	1.8	107.5
13	BC_1	225 280	563 220	2.5	84.9
16	BC_2	773 400	1 701 480	2.2	83.7
21	BC_3	24 739	231 660	9.4	149.2
22	BC_4	12 689	153 530	12.1	131.1
25	BC_5	8426	95 987	11.3	138.3
30	BC_6	9202	91 567	10.0	139.2
32	BC_7	23 736	154 832	6.5	143.6

[a] Extracted from HT-GPC-IR data. [b] The samples selected based on the highest M_v obtained for each catalyst.

were $BC_1 > MC_1$, $BC_4 > MC_2$ and $BC_2 > MC_3$. The synergistic effect of the dinuclear catalysts could depend on the structure of the bridging ligand, as well as on the relative distance between the two metal centers. This trend, in terms of the electronic and steric effects, can be modulated by using flexible or rigid groups with different bridge lengths. The higher activities of BC_5 and BC_7 than those of BC_3 and BC_6, respectively, imply that the greater electron density delivered by the longer phenyl or methylene bridge stabilizes the active sites and accelerates the rate of polymerization.[25–27] By considering the obtained M_v, M_w and MWD values of the poly-(1-hexene) samples, the effect of catalyst structure on molecular features is revealed. Whereas the mononuclear catalysts just produce high molecular weight fractions with narrow MWD, the dinuclear catalysts polymerize 1-hexene from a high molecular weight polymer with narrow MWD to a mixture of low and high molecular weights and broad to bimodal MWD.

For the mononuclear catalysts, the single site nature of catalyst leads to a narrow MWD (1.8–2.1) (Fig. 4A and Table 3).
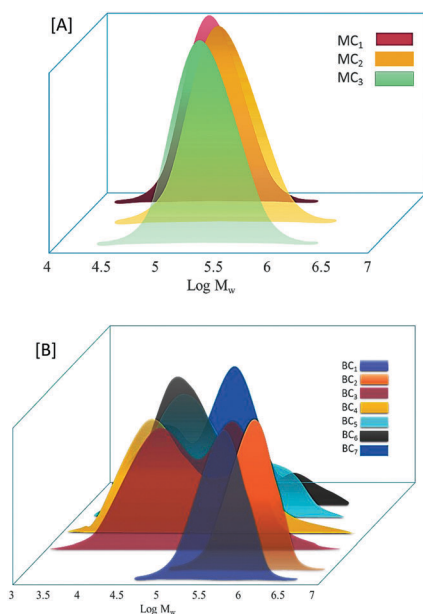

Fig. 4 GPC curves of poly(1-hexene) samples produced using the [A] mono- and [B] dinuclear catalysts.

This effective steric and hindering influence of the structure could also be observed in BC1 and BC_2 (MWDs = 2.5 and 2.2). In contrast, a broad to bimodal MWD was observed for BC_3–BC_7 (Fig. 4B and Table 3). This observation implies that there is more than one type of active site for polymerization.[6,11,28] The two possible stereoisomers (syn and anti) lead to two different positions of active centers. In other words, one can polymerize 1-hexene into low M_w and the other into higher M_w.[12,29] To clarify, in dinuclear structures (BC_3–BC_7), the presence of the ortho-substituent only on one side of each center results in less-effective shielding through the bridge between the Ni centers. This point is a reason for the high rate of chain transfer reactions and the production of low molecular weight fractions. More details on the stereoisomers are currently being explored.

Besides, the probable explanation for the production of higher molecular weight poly(1-hexene) is trapping of monomers or oligomers effects due to the agostic interaction leading to the positive incorporation of two adjacent metal centers in the bimetallic catalysts and optimum bulkiness.[6,30–33] The longer bridge in BC_5 indicating a higher distance between the centers in comparison to BC_3 led to a broader MWD due to less steric and cooperative effects on the Ni centers. For BC_7, however, the greater cooperative effect led to a higher fraction of high molecular weight and narrow MWD. These points can also be observed in the GPC curves with the portions of low and high molecular weights of poly(1-hexene) in regards to the structure. In addition, the GPC-IR (Table 3) data showed that the poly(1-hexene) samples obtained by BC_1 and BC_2 have lower branching densities compared to those prepared with $MC_{1–3}$ and $BC_{3–7}$. This can be attributed to the positive synergistic effect of Ni centers along with the steric effect of the bridge leading to a higher level of complete chain walking.[2,14,34]

In conclusion, we investigated the synthesis of high to low molecular weight poly (1-hexene) using a series of mono- and dinuclear Ni-based catalysts by which the effects of structure such as nuclearity, length and nature of the bridge, backbone and ortho-aryl substituent were observed. Dinuclearity along with the efficient electronic and steric effect of the backbone and ortho aryl substituents lead to a greater catalyst activity, lower branching density, higher molecular weight and narrower MWD of the produced polymer (BC_2 and BC_1). The flexibility and

less effective blocking of axial sites by the bridge can lead to lower molecular weight and broader MWD and a higher level of branching (BC_{3-7}). The longer distance between the centers ($BC_6 \leftrightarrow BC_7$, $BC_3 \leftrightarrow BC_5$) through the higher electron density delivered by the spacer improves the catalyst activity.

Notes

More details including the microstructure of poly(1-hexene) (branching distribution) and longer α-olefins along with the polymerization parameters, thermal properties, computational investigation of the structures and mechanistic routes will be discussed in our future full paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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