

Nickel cyclopentadienyl complexes as catalysts for ethylene polymerization



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ABSTRACT

Nickel cyclopentadienyl phenyl phosphine complexes $\text{CpNi}(\text{Ph})(\text{PPh}_3)$ (Cp = cyclopentadienyl, and iminoaryl-substituted cyclopentadienyl) are used as catalysts for ethylene polymerization in the presence of methylaluminoxane (MAO). The catalytic performances were studied under a variety of reaction conditions in which Al/Ni molar ratio, ethylene pressure, temperature, time and catalyst loading were varied. The catalytic activities and the molecular weights increase with increasing Al/Ni molar ratio and ethylene pressure. The catalysts are thermally stable. Even at 76 °C, the activity reaches to 109.0 kg PE $(\text{mol Ni})^{-1}\text{h}^{-1}$ with the molecular weights of $M_n = 20.6 \times 10^4$. The effect of the bulkiness of cyclopentadienyl ligands on ethylene polymerization was also investigated. The catalytic activities and the molecular weights of polyethylene decrease as the iminoaryl substituents are introduced into the cyclopentadienyl ring. The polymers obtained from these catalysts are linear polyethylene with 6–8 branches per thousand carbons.

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1. Introduction

Oligomerization and polymerization of α -olefins promoted by nickel catalysts have attracted a great deal of interest in the last decades [1–3]. Most notable are Brookhart's α -diimine nickel and palladium catalysts [4–6], as well as Grubbs' neutral salicylaldehyde nickel (II) catalysts (Fig. 1) [7–9]. The key features of these catalysts are the ligands, which possess rigid frameworks bearing one or two weakly coordinating imino-groups. Like the α -diimine nickel complexes, the incorporation of ortho aryl substituents that lie perpendicular to the square coordination plane was to efficiently shield the center metal from β -H elimination reaction to generate high molecular weight polyethylene, while the absence of those substituents only lead to the oligomers. More recently, a "sandwich-like" 8-p-tolyl naphthyl α -diimine nickel complexes, in which the 8-substituent is ideally positioned to provide steric bulk at the axial sites, can yield the most highly branched polyethylene [10].

On the other hand, cyclopentadienyl (Cp) and substituted derivatives usually used in Group IVB complexes because of the easy coordination and modification by substitution, the application to group 10 metal complexes remained relatively poorly explored,

only a few examples dealing with cyclopentadienyl (Cp) type of nickel catalysts have been reported and most of them for ethylene oligomerization. For example, Matt and his colleagues reported that pentaphenylcyclopentadienyl nickel complexes with chelating hybrid P'O ligands behaved as effective catalysts for low-pressure oligomerization of ethylene in the presence of sodium borohydride [11,12]. The reported results suggested that, when a stronger chelating hybrid P'O ligand was present, the cyclopentadienyl group was displaced from the above catalysts by ethylene to form a hydride species with a vacant coordination site, the sole responsible of the catalytic performances. Sbrana et al. [13] found that homogeneous cyclopentadienyl nickel catalysts displayed good activity for ethylene oligomerization, while the heterogeneous catalysts, synthesized by anchoring the nickel derivative to a styrene/divinylbenzene resin, initiated ethylene polymerization, leading to high density polyethylene instead of oligomerization. They believed that the cyclopentadienyl ligand should remain bonded to the nickel atom during the catalytic cycle, the cyclopentadienyl nickel hydride moiety was proposed as the active species, responsible for α -olefins oligomerization. However, Yasuda and his co-workers reported that nickel complexes such as $(\text{C}_5\text{H}_5)\text{Ni}(\eta^3\text{-allyl})$, activated with modified methylaluminoxane (MMAO), showed no catalytic activity for polymerization of ethylene and 1-olefins although it exhibited high catalytic activity

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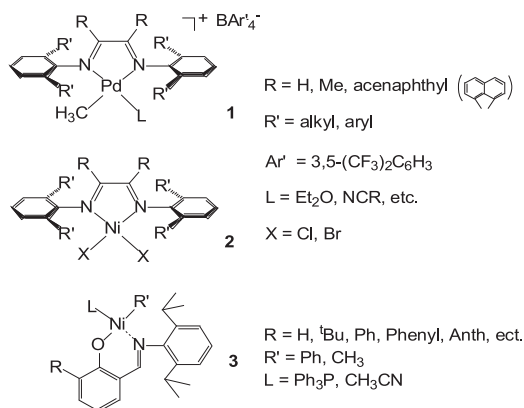


Fig. 1. α -diimine palladium and nickel catalysts, neutral salicylaldimine nickel (II) catalysts.

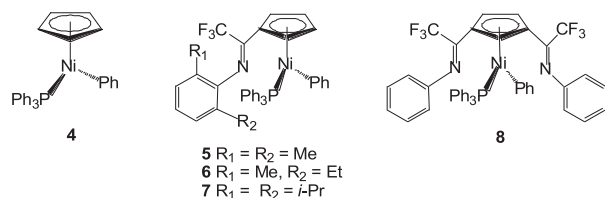


Fig. 2. The structure of the complexes 4–8.

for the polymerization of methyl methacrylate (MMA) [14]. The related indenylnickel(II) complexes $[\text{Ni}(\text{Ind})(\text{L})\text{X}]$ (Ind = indenyl; L = 1,3-diisopropylimidazole-2-ylidene; X = Cl or Br), studied by Shen's group, with methylaluminumoxane (MAO) as a co-catalyst, displayed modest activity in dimerization of ethylene with a high selectivity [15]. The products 1-butene indicated that β -H elimination from the putative Ni-Bu intermediate was too fast for chain propagation. They suggested that the high selectivity of the two NHC complexes for ethylene dimerization might be due to the facile reductive elimination of the alkyl group from Ni(II) N-heterocyclic carbene complexes [16]. Pietrzykowski et al. [17] also reported that cyclopentadienylnickel(II) complexes with N-heterocyclic carbenes $[\text{NiCp}(\text{X})(\text{NHC})]$ (X = Cl, Br or CH_3), combined with MAO, revealed activity for the polymerization of styrene. On the other hand, substituted indenyl–nickel complexes $[\text{Ni}(\text{R-Ind})\text{X}(\text{PR}_3)]$, developed by Zagarin's group, were active catalysts for alkyne polymerization [18], dimerization and polymerization of ethylene [19],

polymerization of styrene [20–22]. The polyethylene obtained from $[\text{Ni}(\text{R-Ind})\text{X}(\text{PR}_3)]/\text{MAO}$ was mostly linear polyethylene which contain a small number of ethyl branches and exhibit molecular weights in the range of $M_w = 10^5$.

We have previously developed a family of nickel iminoaryl-substituted cyclopentadienyl phenyl phosphine complexes. The structures of the complexes (4–8) are illustrated in Fig. 2. These cyclopentadienyl-imino ligands are readily prepared and derivatized, and in addition, they exhibit good thermal stability. In seeking to develop new late-metal olefin polymerization/copolymerization catalysts, several monomers polymerization have been examined and show a good catalytic activity for styrene polymerization [23]. In this contribution, we report the catalytic activity of the complexes for ethylene polymerization in the presence of MAO.

2. Results and discussion

2.1. Ethylene polymerization

Ethylene polymerizations were carried out by activation of the complexes 4–8 in toluene using methyl alumoxane (MAO), and generate high molecular weight polyethylene. Results of polymerization are summarized in Tables 1 and 2.

Table 1 summarizes polymerizations by the complex 4 through varying reaction conditions, such as the molar ratio of MAO to Ni complex (Al/Ni), pressure of ethylene, temperature, time and catalyst loading. It reveals that the molar ratio of Al/Ni and polymerization temperature have much more pronounced influence on catalytic activities and the molecular weights than the ethylene pressure. MAO is essential to ethylene polymerization (entries 1–4 in Table 1). Without MAO, the polymerization is not occurred. When the molar ratio of Al/Ni was lower than 130, almost no polymer was produced. The optimum of the molar ratio of Al/Ni is 500, the catalytic activity reaches $26.5 \text{ kg PE (mol Ni)}^{-1}\text{h}^{-1}$ and the molecular weight of PE is $17.8 \times 10^4 (M_n)$ (entry 3). With more or less 500 of the molar ratio of Al/Ni, the catalytic activities and the molecular weights of PE decrease. Molecular weight distributions of $M_w/M_n \approx 3.0$ indicate a single-site polymerization behavior. Note that molecular weights are analyzed by two ways. Viscosity – average molecular weights (M_n) are calculated from the equation $[\eta] = 6.67 \times 10^{-4} M_n^{0.67}$, the inherent viscosity of polyethylene $[\eta]$ are determined in 1,3,5-trichloro-benzene at 135°C . Number – average molecular weights (M_n) was obtained from gel permeation chromatography (GPC) analyses in 1,3,5-trichloro-benzene at 135°C by comparison with a linear polystyrene standard.

Table 1
Ethylene polymerization with the complex 4/MAO.^a

Entry	Complex/ μmol	Al/Ni	$P_{\text{C}_2\text{H}_4}/\text{atm}$	$T_p/^\circ\text{C}$	Time/hr	Activity ^b	$M_n \times 10^{-4c}$	$M_n \times 10^{-4d}$	PDI ^d
1	40	130	28	45	1	1.0	n. d.	n. d.	n. d.
2	40	300	28	45	1	9.5	8.0	27.1	3.4
3	40	500	28	45	1	26.5	17.8	28.1	3.0
4	40	750	28	45	1	7.3	13.7	n. d.	n. d.
5	20	500	10	45	0.5	16.2	39.1	n. d.	n. d.
6	20	500	20	45	0.5	20.0	44.5	45.9	3.3
7	20	500	28	45	1	18.5	46.2	n. d.	n. d.
8	20	500	20	32	0.5	2.0	n. d.	n. d.	n. d.
9	20	500	20	60	0.5	59.0	32.3	28.1	2.5
10	20	500	20	76	0.5	109.0	28.9	20.6	2.1

n.d., not determined.

^a Polymerization conditions: activation with 10 wt.% MAO in toluene, polymerization in 50 mL toluene.

^b The activities $[\text{kg PE (mol Ni)}^{-1}\text{h}^{-1}]$ were calculated from the total obtained of polyethylene.

^c Viscosity – average molecular weights calculated from the equation $[\eta] = 6.67 \times 10^{-4} M_n^{0.67}$, the inherent viscosity of polyethylene was determined in 1,3,5-trichloro-benzene at 135°C .

^d M_n and PDI were determined by High temperature gel permeation chromatography (GPC), which were run in 1, 2, 4-trichlorobenzene at 135°C using a PL220 GPC equipped with PLgel MIXED-B column, $10 \mu\text{m}$ particle size, 300 mm long.

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