Copolymerization

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Double-Decker-Type Dinuclear Nickel Catalyst for Olefin Polymerization: Efficient Incorporation of Functional Co-monomers**

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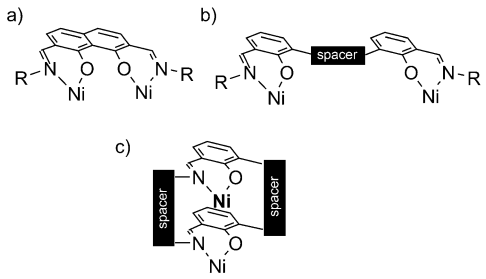
The ethylene polymerization and copolymerization of olefins catalyzed by dinuclear transition-metal complexes have recently attracted recent attention.[1] Both early- and late-transition-metal complexes with a dinuclear structure lead to an increase in the molecular weight in ethylene polymerization and in the co-monomer content for the copolymerization of ethylene with various co-monomers.[2] The stabilization of the growing polymer end and coordination of the co-monomer are efficient in the bimetallic system.[3] Marks and co-workers synthesized a planar dinickel complex, which is supported by an aromatic bis(salicylaldimine) ligand (Scheme 1 a),[4] and found that copolymerization of ethylene

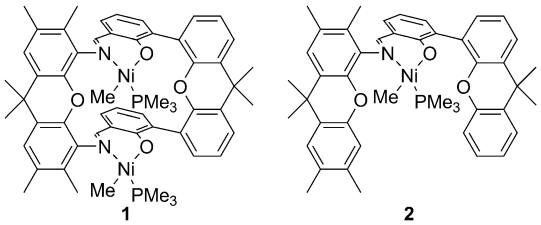


Scheme 1. Three classes of dinuclear salicylaldimine nickel catalyst for olefin polymerization.

with functionalized norbornenes and acrylates resulted in greater incorporation of the co-monomers than that with a mononuclear catalyst.[5] The catalysts, composed of the two nickel salicylaldimine centers and a spacer to join them, have been reported by several research groups independently (Scheme 1 b).[6] The polymer properties are influenced by the distance between nickel centers. Agapie and co-workers investigated olefin polymerization using their dinuclear complexes and revealed a dimer effect in inhibition of the catalysis by amine additives.[7] Lee and-co-workers reported the dinickel complex supported by a macrocyclic salicylaldimine ligand with a Ni···Ni separation of 8.869 Å (Scheme 1 c) and a moderate catalytic activity for ethylene polymerization.[8]

We designed a dinuclear nickel catalyst supported by a rigid macrocyclic ligand, which forces the two nickel centers into close proximity, closer than reported for other catalysts so far. The catalyst is expected to show unique properties not only in ethylene polymerization but also in copolymerization with functionalized monomers, such as terminal dienes,[9] owing to the synergistic effects of the two metal centers. Herein, we show the synthesis of a new dinickel catalyst as well as its application in olefin polymerization.

The dinuclear nickel complex **1** and its mononuclear analogue **2** are obtained from the reaction of deprotonated ligand precursors with $[(Me_3P)_2NiMeCl]$.[10] The molecular



structure of **1**, determined by X-ray crystallography (Figure 1), indicates that the methyl and PMe_3 ligands bonded to the two metal centers are positioned on the same side of the xanthene planes. The two nickel centers of **1** are separated by 4.73 Å, which is shorter than that in the previously reported dinuclear salicylaldimine nickel complexes (5.80–8.9 Å).[5c,6d,7,8]

Both **1** and **2** catalyze ethylene polymerization in the presence of a $[Ni(cod)_2]$ (cod = cyclo-1,5-octadiene) co-catalyst, which serves as a phosphine scavenger. The two complexes, however, differ significantly in the catalytic activity (2.1 g mmol Ni^{-1} h^{-1} atm^{-1} for **1** and 0.37 g mmol

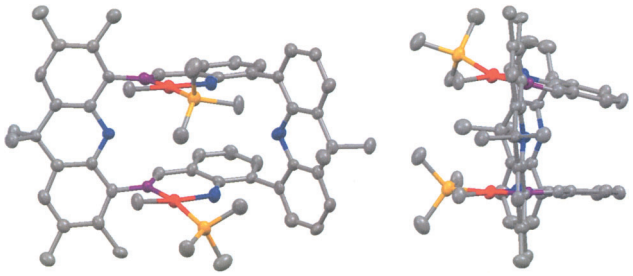


Figure 1. Structure of **1** determined by X-ray crystallography. Hydrogen atoms are omitted for clarity.

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Table 1: Polymerization and copolymerization of ethylene by dinuclear and mononuclear salicylaldimine nickel catalysts.[a]

Entry	Co-monomer	Cat.	Yield [mg]	Activity [g mmolNi^{-1} h^{-1} atm^{-1}]	Branches per 1000 C	Incorp. [mol%]	M_w[b]	M_w/M_n[b]
1	–	**1**	317	2.1	59	–	12000	4.5
2[c]	–	**2**	55.4	0.37	95	–	1700	1.8
3	1-hexene	**1**	416	2.8	56	–[d]	13900	3.8
4	1,5-hexadiene	**1**	16.7	0.1	53	–[d]	6900	2.4
5[c]	1,5-hexadiene	**2**	4.5	–	95	–	–	–
6	1,6-heptadiene	**1**	160	1.1	29	3.6	40000	4.1
7	1,7-octadiene	**1**	149	1.0	31	–[d]	57400	7.5[f]
8[e]	1,7-octadiene	**1**	62.3	0.4	38	2.0	21300	4.7
9[c]	1,7-octadiene	**2**	20.4	0.1	110	–	–	–
10	2,2-diallyl-5,5-dimethyl-1,3-dioxane	**1**	303	2.0	46	1.8	21800	4.2
11[c]	2,2-diallyl-5,5-dimethyl-1,3-dioxane	**2**	trace	–	–	–	–	–
12	*tert*-butyl butenoate	**1**	2.6	0.02	35	1.4	–[d]	–[d]
13	ethyl pentenoate	**1**	8.2	0.05	32	0.4	17500	6.5[f]
14	methyl acrylate	**1**	trace	–	–	–	–	–
15	5-norbornene-2-carboxylic acid methyl ester	**1**	38.0	0.25	70	4.1	30600	8.2

[a] Reaction conditions: **1** = 10 μmol, [Ni(cod)$_2$] = 40 μmol, ethylene = 5 atm, co-monomer = 4.5 mmol, solvent = toluene (25 mL), at RT, 90 min, unless otherwise noted. [b] Determined by GPC detected by IR based on polyethylene standard using *o*-dichlorobenzene as eluent at 140 °C. [c] **2** = 20 μmol. [d] Not determined. [e] Co-monomer = 9.0 mmol. [f] Bimodal molecular weight distribution.

$Ni^{-1}h^{-1}atm^{-1}$ for **2**). The polyethylene produced from **1**/[Ni(cod)$_2$] has a methyl-branched structure and a higher molecular weight (M_w = 12000), and polymerization catalyzed by **2**/[Ni(cod)$_2$] yields a methyl- and ethyl-branched polymer with M_w = 3100. Marks and co-workers reported that their planar dinickel catalyst affords polyethylene with selective formation of a methyl-branched polymer. The fractionation of the former polyethylene resulted in *n*-hexane-soluble and *n*-hexane-insoluble fractions in a 88:12 weight ratio.[11]

Table 1 summarizes the results of ethylene polymerization (entries 1 and 2) and copolymerization of ethylene with α-olefin, terminal dienes, and unsaturated esters. The polymerization of ethylene (5 atm) in the presence of 1-hexene (1-hexene/Ni = 225) catalyzed by **1**/[Ni(cod)$_2$] (**1** = 10 μmol, [Ni(cod)$_2$]/**1** = 4) is not retarded by the co-monomer (entry 3), although the late-transition-metal-catalyzed copolymerization of ethylene and α-olefin often suffers from a significant decrease in the polymerization rate and polymer yields compared with ethylene polymerization.[4b,7b] The $^{13}C\{^1H\}$ NMR spectrum of the polymer contains a signal resulting from the methyl branch (δ = 20.0 ppm) and a much smaller signal corresponding to the ethyl branch (δ = 11.1 ppm), and signals for propyl or butyl branches are not observed (Figure 2b).[7b,12] The molecular weights of the polymers are similar for the reactions with and without 1-hexene (M_w = 13900 and 12000). These results suggest that 1-hexene in the reaction mixture does not affect the polymerization rate and is not incorporated into the polymer. In contrast, the addition of 1,5-hexadiene to the polymerization mixture of ethylene catalyzed by **1**/[Ni(cod)$_2$] causes a significant decrease in the activity (entry 4).

In contrast, **1** and [Ni(cod)$_2$] catalyze the smooth copolymerization of ethylene with 1,6-heptadiene to afford the polymer with M_w = 40000 (M_w/M_n = 4.1; Table 1, entry 6). The $^{13}C\{^1H\}$ NMR spectrum of the polymer (Figure 2c) shows the signals labeled *a*–*e*, which are not observed in the spectrum of polyethylene (Figure 2a). They are assigned to the -CH_2-C_5H_8-CH_2- group containing a 1,2-*trans* five-membered ring, as the shifts are similar to those for an ethylene-1,6-heptadiene copolymer obtained using a cobalt catalyst.[9k] The relative intensity of the ^1H NMR signal of the CH hydrogen (δ = 1.77 ppm), relative to those of CH_3, CH_2, and CH hydrogen atoms, which results from the methyl-branched ethylene units indicates the incorporation of the diene unit at 3.6 mol% of total repeating units.

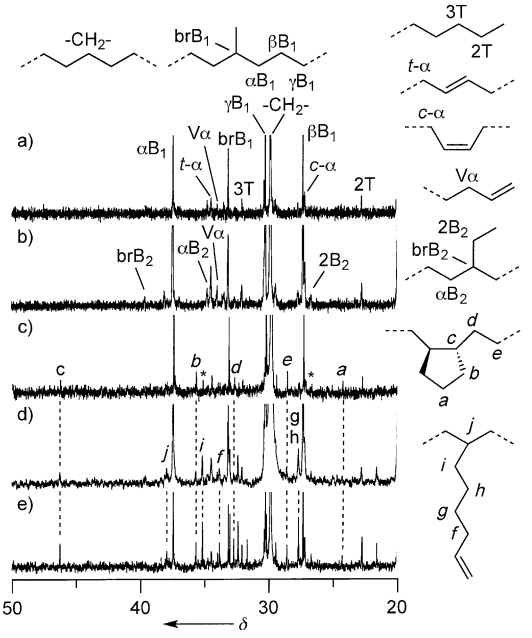


Figure 2. $^{13}C\{^1H\}$ NMR spectra ($C_2D_2Cl_4$ at 130 °C) of the polymers obtained using the **1**/[Ni(cod)$_2$] catalyst. a) Entry 1, b) entry 3, c) entry 6, d) entry 7, and e) entry 8 in Table 1.

The copolymerization of ethylene with 1,7-octadiene catalyzed by **1**/[Ni(cod)$_2$] also affords a copolymer, whose

activity decreases with an increase in the amount of the added diene (Table 1, entries 7 and 8). The $^{13}C\{^1H\}$ NMR spectrum shows signals corresponding to the -CH_2-CH_2- repeating unit, methyl branch, and -CH_2-C_5H_8-CH_2- repeating unit, similar to the case of the ethylene-1,6-heptadiene copolymer (Figure 2d,e). The polymer contains neither a 1,2-disubstituted cyclohexane ring[13] nor a 1,3-disubstituted cycloheptane ring,[14] which would show signals at $\delta = 42.6$ (1,2-CH) and 42.8 ppm (2-CH_2), respectively. The ^1H NMR spectrum of the copolymer shows signals corresponding to the vinylene (-CH=CH-) and vinyl (=CH_2) groups at $\delta = 5.40$ and 4.96 ppm, respectively. The intensity ratio of the signals, 0.63:1, is larger than that of polyethylene (0.22:1) and the ethylene-heptadiene copolymer (0.21:1), thus suggesting that part of 1,7-octadiene is incorporated without cyclization to yield the repeating unit with a pendant olefin.

The polymerization of ethylene in the presence of 1,7-octadiene catalyzed by **2**/[Ni(cod)$_2$] yields the product in a much smaller amount (20 mg; Table 1, entry 9) compared to that obtained with **1**/[Ni(cod)$_2$]. The polymer does not contain the cyclic group (-CH_2-C_5H_8-CH_2-) or the pendant vinyl group.

The GPC analysis of the ethylene-1,7-octadiene copolymer (Table 1, entry 7) shows a bimodal molecular weight distribution, while that of the polyethylene obtained using the same catalyst shows a unimodal elution (Figure 3a). The

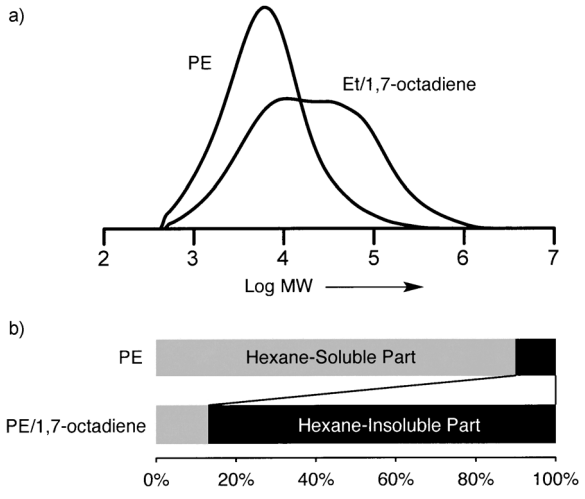


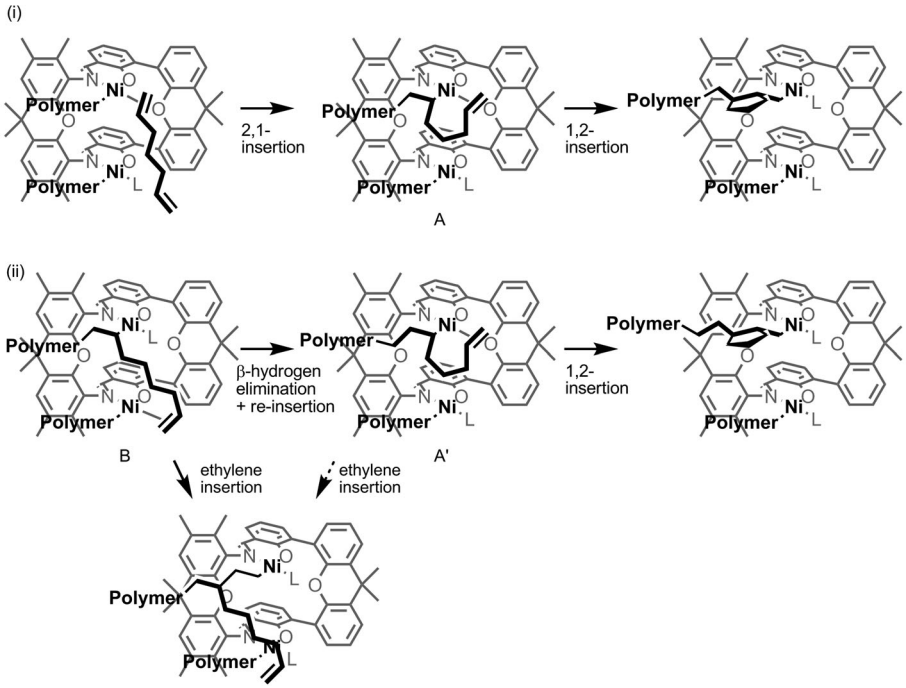
Figure 3. a) GPC profiles and b) weight fraction of *n*-hexane-soluble and *n*-hexane-insoluble parts after Soxhlet extraction of polyethylene (Table 1, entry 1) and ethylene-1,7-octadiene copolymer (Table 1, entry 5) obtained using **1**/[Ni(cod)$_2$].

higher-molecular-weight fraction of the copolymer is eluted earlier than polyethylene obtained using the same catalyst. The Soxhlet extraction of the copolymer indicates the presence of 87% of an *n*-hexane-insoluble fraction (Figure 3b). The ethylene-1,6-heptadiene copolymer also contains an *n*-hexane-insoluble fraction as the major component (82%). This data is in contrast to the results of homopolyethylene, which contains the insoluble fraction as a minor component (12%). The lower solubility and higher molecular weight of the copolymers relative to the polyethylene suggest a partially crosslinked structure. Although a copolymer of ethylene with terminal dienes was reported to form crosslinked copolymers, which are insoluble in common organic solvents even at high temperature,[15] the copolymer obtained using the dinickel catalyst is soluble in 1,1,2,2-tetrachloroethane at 130°C. This outcome is probably because the crosslinking is less significant than that obtained using the common mononuclear catalyst. The $^{13}C\{^1H\}$ NMR spectra of ethylene-1,6-heptadiene and ethylene-1,7-octatadiene copolymers showed small signals at $\delta = 35.1$ ppm and 27.1 (marked with asterisks in Figure 2c), which may be due to the crosslinked structure,[15h] although the signal of the ethylene-1,7-octadiene copolymer overlaps with other signals.

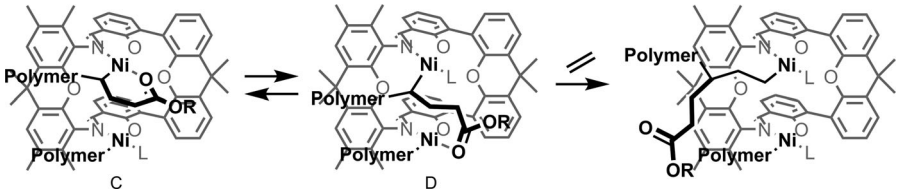
The copolymerization of ethylene with 2,2-diallyl-5,5-dimethyl-1,3-dioxane yields 302.8 mg of the polymer (Table 1, entry 10).[16] The repeating unit of the diene monomer is calculated to be 1.8 mol% of the monomer units. The ^1H NMR spectrum suggests a structure without cyclization (see Figure S-6 in the Supporting Information).[17] The dinuclear nickel complex also promotes the copolymerization of ethylene with butenoate and pentenoate (entries 12 and 13). ^1H NMR signals at $\delta = 2.16$–2.25 ppm (triplet) and $\delta =$ 1.56–1.60 ppm (multiplet) are assigned to the ethylene group between the alkoxycarbonyl group and the polymer chain. The absence of signals in the region of $\delta = 1.5$–1.7 ppm suggests that the polymer does not contain an alkoxycarbonyl propyl substituent.[18]

Scheme 2 shows a summary of the polymer growth of the copolymerization of ethylene with 1,6-heptadiene and 1,7-octadiene catalyzed by **1**/[Ni(cod)$_2$]. The 2,1-insertion of a vinyl group of 1,6-heptadiene into the Ni–polymer bond forms the intermediate **A**. The subsequent 1,2-insertion of the terminal vinyl group leads to the five-membered ring, as shown in Scheme 2a. 1,7-Octadiene undergoes the initial 2,1-insertion of a vinyl group, thus giving **B** (Scheme 2b). The migration of the alkyl group attached to the Ni center of **B** should occur to afford **A**′, which is responsible for formation of the five-membered ring. Ethylene insertion into the Ni–C bond of either **B** or **A**′ produces a monomer unit with a terminal vinyl group. The intermediates **A** and **A**′ are stabilized by the coordination of the pendant vinyl group to the other Ni center. 1-Hexene is not involved in the polymerization in the presence of ethylene because of its much lower affinity to the dinuclear catalyst than the 1,6- and 1,7-dienes. Ma and co-workers reported the acyclic dititanium catalyst enhances incorporation of 1,5-hexadiene in copolymerization with ethylene and forms the polymer with higher density of the cyclized units than the polymer from mononuclear catalyst.[2e] Selectivity or different reactivity of the diene monomers, however, was not investigated.

The copolymerization of ethylene with the esters of alkenyl carboxylic acids involves the 2,1-insertion of the monomer and isomerization to give a stable six-membered chelate intermediate (**C**; Scheme 3). Although such an intermediate tends to suppress further insertion of ethylene to its Ni–C bond,[5b] the presence of the other Ni center in the catalyst molecule allows opening of the six-membered chelate ring, thus giving **D**, which undergoes smooth insertion of ethylene into the Ni–polymer bond.



Scheme 2. Plausible mechanism of the chain growth in the copolymerization using a) 1,6-heptadiene and b) 1,7-octadiene as the co-monomer catalyzed by **1**/[Ni(cod)$_2$].



Scheme 3. Plausible mechanism of the chain growth in the copolymerization of ethylene with unsaturated esters catalyzed by **1**/[Ni(cod)$_2$].

In summary, a dinuclear nickel complex with a double-decker structure promotes the copolymerization of ethylene with bifunctional co-monomers. Both terminal dienes and unsaturated esters, with three or four carbon atoms between vinyl and/or oxygen atoms, are suitable for the reaction catalyzed by **1**/[Ni(cod)$_2$]. The close proximity of the Ni centers (ca. 4.7 Å), supported by the rigid macrocyclic ligand, enhanced the coordination of the bifunctional monomers and stabilized the growing polymer end on one nickel center by coordination of the vinyl or carbonyl group to the other nickel center. Di-nickel catalysts with different Ni–Ni distances and different substituents on the cyclic ligand should enable the selective copolymerization of ethylene with other various bifunctional co-monomers.

Experimental Section

General procedure for copolymerization by **1**/[Ni(cod)$_2$]: A toluene solution (10 mL) containing **1** (10 μmol) and [Ni(cod)$_2$] was added to a 50 mL autoclave containing a toluene solution (15 mL) of co-monomer (4.5 mmol) under an ethylene atmosphere. The reaction mixture was stirred at room temperature under 5 atm of ethylene. After 90 min, the reaction mixture was poured into HCl/methanol (1:4; ca. 100 mL). The solid formed was collected and dried in vacuo at 25 °C to give the copolymer.

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