Polymerization

Deutsche Ausgabe: DOI: 10.1002/ange.201510077
Internationale Ausgabe: DOI: 10.1002/anie.201510077

Copolymerization of Ethylene and Polar Monomers by Using Ni/IzQO Catalysts

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Abstract: *The replacement of precious metals in catalysis by earth-abundant metals is currently one of the urgent challenges for chemists. Whereas palladium-catalyzed copolymerization of ethylene and polar monomers is a valuable method for the straightforward synthesis of functionalized polyolefins, the corresponding nickel-based catalysts have suffered from poor thermal tolerance and low molecular weight of the polymers formed. Herein, we report a series of neutral nickel complexes bearing imidazo[1,5-a]quinolin-9-olate-1-ylidene (IzQO) ligands. The Ni/IzQO system can catalyze ethylene polymerization at 50–100 °C with reasonable activity in the absence of any cocatalyst, whereas most known nickel-based catalysts are deactivated at this temperature range. The Ni/IzQO catalyst was successfully applied to the copolymerization of ethylene with allyl monomers to obtain the corresponding copolymers with the highest molecular weight reported for a Ni-catalyzed system.*

Since the seminal discovery by Brookhart and co-workers in 1996,[1] the coordination–insertion copolymerization of olefins with polar monomers by Group 10 metal catalysts bearing a bidentate ligand (Figure 1) has attracted great attention as a straightforward method for the preparation of high-value polyolefins with improved properties such as adhesiveness, dyeability, printability, and compatibility.[2] Although palladium-based catalysts, such as Pd/α-diimine **1-Pd**,[1] Pd/phosphine–sulfonate **2-Pd**,[2e,f,3,4] and Pd/bisphosphine monoxide,[5] have demonstrated a unique ability to produce olefin/polar monomer copolymers, their high cost owing to the use of a precious metal may hinder their industrial application.[2,6] Hence, the replacement of palladium with the more abundant and less expensive nickel has been examined, leading to the development of nickel catalysts,[6] for example, **1-Ni**,[1,7–9] **2-Ni**,[10,11] **3**,[12,13] **4**,[14–17] **5**,[18] and **6-Ni**[19] (Figure 1).[2e,20,21]

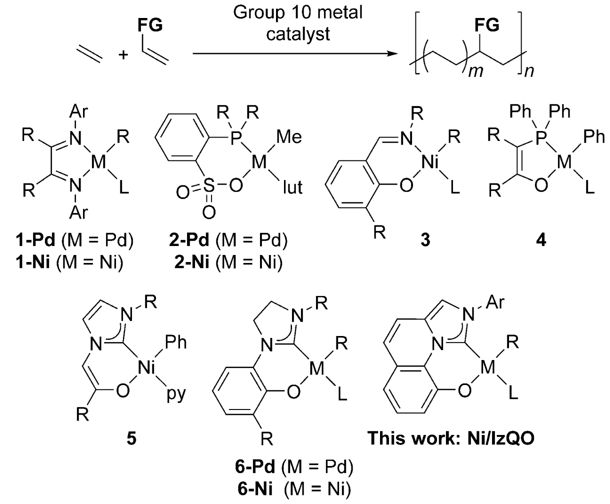

Figure 1. Representative Group 10 metal catalysts investigated for olefin (co)polymerization (M = Pd or Ni). lut = 2,6-lutidine; py = pyridine.

Compared with palladium-based catalysts, the corresponding nickel-based catalysts suffer from several critical drawbacks, such as 1) poor temperature tolerance[22], 2) low molecular weight of the obtained (co)polymers, and 3) heavier suppression by polar monomers, which undermine their economic value. Because olefin polymerization is a highly exothermic reaction, processes requiring low temperatures are difficult to control and their use of thermal drain is less efficient. As exemplified in the well-known shell higher olefin process (SHOP),[14] nickel catalysts undergo β-hydride elimination followed by chain transfer, which often forms undesired co-oligomers of the olefin/polar monomer. Although nickel catalysts are generally more active for olefin homopolymerization than the corresponding palladium catalysts,[1a] in the presence of large amounts of polar monomers, their catalytic activity is significantly reduced or even suppressed because of the more highly oxophilic nature of the nickel center.[1b,9] The scope of polar monomers with nickel-based catalysts is thus narrower than that with palladium; only co-oligomerization or copolymerization with methyl acrylate,[9,17,21c] amino olefins,[13c] functionalized norbornenes,[13a,20b] and other comonomers,[8] and co-oligomerization with allyl acetate and allyl silyl ether[11] have thus far been accomplished. It should be noted, however, that most examples often suffer from low molecular weight of the polymer formed; for example, $M_n < 2000$ for methyl acrylate[21c] and $M_n < 1000$ for allyl acetate.[11]

Recently, we reported palladium complexes bearing imidazo[1,5-*a*]quinolin-9-olate-1-ylidene ligands (Pd/IzQO), which can polymerize α-olefins while incorporating polar monomers.[23] Whereas the known Group 10 metal polymerization catalysts **5**[18] and **6-Pd**,[24] which bear N-heterocyclic carbene (NHC)-based ligands, decompose rapidly under the polymerization conditions, the Pd/IzQO catalyst is stable because of its structural confinement, wherein the NHC plane is coplanar to the metal square plane. The thermal stability at

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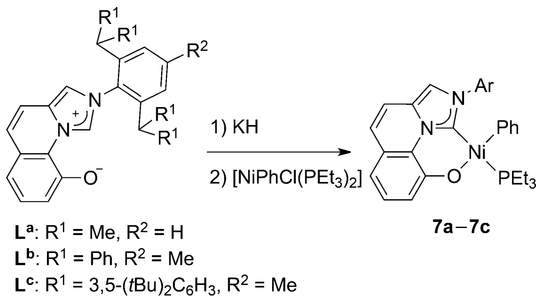
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510077.

temperatures above 100 °C and the high molecular weight of the obtained polyethylene were comparable to the best values achieved with the previously optimized systems, such as Pd/phosphine–sulfonate catalysts **2-Pd**. Moreover, Pd/IzQO catalysts do not require high concentrations of polar monomers for effective incorporation; their incorporation affinity toward polar monomers over ethylene was 5–10 times higher than that of Pd/phosphine–sulfonate catalysts **2-Pd**, and polyethylene with comparable molecular weight is produced. In light of the above-mentioned issues regarding nickel-based catalysts, we envisioned that IzQO ligands might be well suitable for complexing nickel ions.

The synthetic procedure for Ni/IzQO complexes is summarized in Scheme 1. An initial attempt using [(tmeda)-$NiMe_2$] (tmeda = *N*,*N*,*N*,*N*-tetramethylethylenediamine) and imidazolium salt **L**^{a} in the presence of pyridine or 2,6-lutidine afforded a mixture of the desired pyridine- or 2,6-lutidine-coordinated complexes [(C^O)NiMeL] and an oxygen-bridged nickel methyl dimer [{(C^O)NiMe}$_2$]. Therefore, a stronger neutral ligand PEt_3 was used, as reported by Grubbs et al. for the synthesis of related complexes **6-Ni**.[19] Treatment of [NiPhCl(PEt_3)$_2$] with deprotonated carbene salts afforded nickel complexes [(C^O)NiPh(PEt_3)] (**7a**–**c**) selectively. The solid-state structure of complex **7a** was confirmed by X-ray crystallography (Figure 2).[25] Similarly to previously reported nickel complexes **3**, **5**, and **6-Ni**, because of the strong *trans* effect of the NHC moiety, the carbene was located in the *trans* position through weak coordination with PEt_3. The Ni–C1 and Ni–O1 bond lengths (1.902(4) Å and 1.908(2) Å, respectively) are slightly longer than those reported by Waymouth and coworkers for complex **5** (1.848(3) Å and 1.891(2) Å, respectively).[18a] The 2,6-diisopropylphenyl ring on the nitrogen atom is nearly perpendicular to the NHC plane, with a dihedral angle of 67.8°. The mean dihedral angle between the NHC plane and the metal coordination square,[23] which corresponds to the averaged torsion angle of the NHC plane from the coordination square, was found to be 32.5° in complex **7a**, which is slightly larger than that in complex **5** (21.9°) and that in the Pd/IzQO complex bearing ligand **L**^{a} (23.6°).



Scheme 1. Synthesis of Ni/IzQO complexes **7a**–**c**.

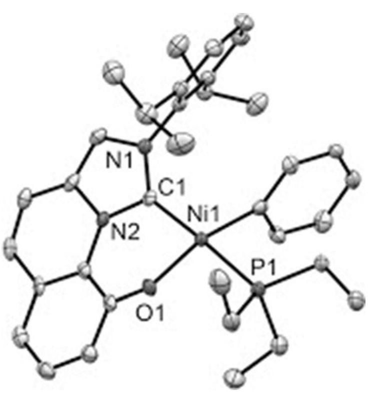


Figure 2. X-ray structure of **7a**. Selected bond lengths [Å]: Ni1–C1 = 1.902(4), Ni1–O1 = 1.908(2), Ni1–P1 = 2.2202(12).

Table 1: Ethylene polymerization by Ni/IzQO complexes **7a**–**c**.[a]

Entry	Cat.	T [°C]	Activity [kg mol^{-1} h^{-1}]	M_n[b] [kg mol^{-1}]	M_w/M_n[b]	Branch[c]
1	**7a**	100	240	2.6	2.3	0
2	**7b**	100	320	6.9	2.3	0
3	**7c**	100	720	16	2.3	0
4	**7c**	80	630	16	2.7	0
5	**7c**	50	340	39	2.1	0
6	**7c**	30	0	–	–	–
7[d]	**7c**	50	1190	54	2.1	0
8[d]	**7c**	30	1000	84	2.0	0

[a] A mixture of catalyst (2.5 μmol) and ethylene (4.0 MPa) in toluene (7.5 mL) was stirred for 0.50 h at the indicated temperature. [b] Number-average molecular weight measured by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. [c] Methyl branches per 1000 C determined by quantitative ^{13}C NMR analysis. [d] A solution of [Ni(cod)$_2$] (5.0 μmol; 2.0 equivalents to the Ni/IzQO catalyst) in toluene (1.0 mL) was added.

With nickel complexes **7a**–**c** in hand, we first investigated their catalytic activity for ethylene polymerization for 0.5 h (Table 1). At 100 °C, which was the optimal temperature for the Pd/IzQO system,[23] nickel complex **7a** can initiate ethylene polymerization without any cocatalyst (entry 1), affording a linear polyethylene with $M_n = 2.6$ kg mol^{-1}. The linear structure of the polyethylene was confirmed by ^{1}H NMR and quantitative ^{13}C NMR analyses; it is noteworthy that no signals attributed to methyl or other alkyl branches were observed in the quantitative ^{13}C NMR spectrum. When using complexes **7b** or **7c**, which bear bulkier substituents on the nitrogen atom (Table 1, entries 2 and 3), the molecular weight (M_n) of the obtained polyethylene increased to 6.9 kg mol^{-1} and 16.0 kg mol^{-1}, respectively. The steric hindrance at the strong σ-donor motif is known to be important for increasing the molecular weight of the polyolefin with the Pd/phosphine–sulfonate catalysts **2-Pd**[4d] and the related NHC-based complex **5**.[18a] When the reaction time was prolonged to 1.0 h, it was found that complex **7a** had lost its activity for ethylene polymerization within 0.5 h at 100 °C. On the other hand, complexes **7b** and **7c** could continue to produce polyethylene after 0.5 h at that temperature, although their catalytic activities were gradually reduced.[26] Then, we investigated the effect of the reaction temperature on the polymerization by using **7c**, which gives the highest molecular weight (Table 1, entries 4–6). When the reaction temperature was lowered to 50 °C,[27] the molecular weight of the polyethylene increased, presumably owing to a decreased rate of chain transfer (Table 1, entries 3–5). At 30 °C, however, **7c** cannot initiate the polymerization (Table 1, entry 6). In the presence of [Ni(cod)$_2$], a well-known phosphine scavenger, **7c** was found to catalyze ethylene polymerization at 50 °C and even at 30 °C (Table 1, entries 7 and 8). Activation by [Ni(cod)$_2$] thus led to an increase in both the catalytic activity (up to 1.19×10^3 kg mol^{-1} h^{-1}; entry 7, 50 °C) and the M_n of the polyethylene (up to 84 kg mol^{-1}; entry 8, 30 °C).

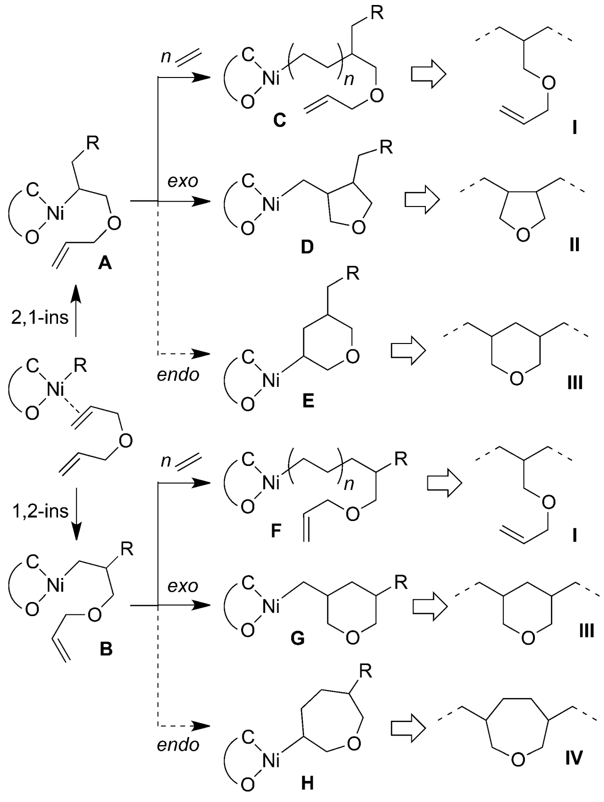
Encouraged by these findings, we investigated the copolymerization of ethylene with polar monomers (Table 2). In the absence of [Ni(cod)$_2$], **7a** catalyzed the co-oligomerization of ethylene with allyl acetate at 100 °C, affording a co-oligomer with M_n 0.63 kg mol^{-1} and 0.49 mol % incorporation of allyl acetate (Table 2, entry 1). It is worth noting that ethylene/allyl acetate copolymerization under similar conditions by the corresponding Pd/IzQO complex afforded the copolymer (M_n of 7.4×10^3 and 1.4 mol % incorporation ratio) with a polymerization activity of 4.5 kg mol^{-1} h^{-1}.[23] Since lowering the reaction temperature led to ethylene homopolymers with higher molecular weight, the copolymerization was carried out at 60 °C using [Ni(cod)$_2$] as cocatalyst (Table 2, entry 2). As expected, the molecular weight of the copolymer increased to 1.5 kg mol^{-1}, with 0.83 mol % of incorporated allyl acetate. Similar to the trend observed in ethylene homopolymerization, complexes **7b** and **7c**, which bear bulky substituents on the nitrogen atom, effectively increased the molecular weight of ethylene/allyl acetate copolymers to 4.5 kg mol^{-1} and 8.5 kg mol^{-1}, respectively; however, the degree of allyl acetate incorporation was significantly lowered to 0.72 mol % and 0.20 mol %, respectively (Table 2, entries 2–4). Nevertheless, higher molecular weight and allyl acetate incorporation could be achieved by using the Ni/IzQO system compared to the values obtained with the Ni/phosphine–sulfonate catalyst **2-Ni**, which generates co-oligomers with M_n up to 1000 and allyl acetate incorporation up to 0.24 %.[11]

Table 2: Copolymerization of ethylene with polar monomers by Ni/IzQO complexes.[a]

Entry	Cat.	Comonomer (mmol)[b]	Activity [kg mol^{-1} h^{-1}]	M_n[c] [kg mol^{-1}]	M_w/M_n[c]	i.r.[d] (mol %)
1[e]	**7a**	AAc (5.0)	0.50	0.63	2.3	0.49
2	**7a**	AAc (20)	0.16	1.5	2.8	0.83
3	**7b**	AAc (20)	0.13	4.5	2.5	0.72
4	**7c**	AAc (20)	0.44	8.5	2.5	0.20
5	**7a**	DAE (16)	0.87	2.8	2.6	1.9
6	**7c**	DAE (16)	0.97	14	3.9	0.98
7	**7a**	AEE (18)	0.88	1.2	2.1	0.68
8	**7c**	AEE (18)	2.1	10	2.1	0.39
9[f]	**7a**	MA (1.0)	0	–	–	–
10[f]	**7a**	AN (1.5)	0	–	–	–

[a] A mixture of **7a**, **7b**, or **7c** (10 μmol), [Ni(cod)$_2$] (20 μmol), a polar monomer (ca. 2.0 mL), and ethylene (3.0 MPa) in toluene (8.0 mL) was stirred for 15 h at 60 °C. [b] AAc = allyl acetate, DAE = diallyl ether, AEE = allyl ethyl ether, MA = methyl acrylate, AN = acrylonitrile. [c] Number-average molecular weight measured by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. [d] Incorporation ratio (i.r.) of polar monomers determined by ^{1}H NMR analysis. [e] Copolymerization was performed with allyl acetate (0.5 mL) in toluene (9.5 mL) at 100 °C in the absence of [Ni(cod)$_2$]. [f] Copolymerization was performed with a polar monomer (0.1 mL) in toluene (10 mL) at 100 °C in the absence of [Ni(cod)$_2$].

Based on these results, we attempted the copolymerization with allyl ethers.[28] Complex **7a** activated by [Ni(cod)$_2$] catalyzed the copolymerization of ethylene with diallyl ether (DAE) and allyl ethyl ether, affording the corresponding copolymers with M_n 2.8 kg mol^{-1} and 1.2 kg mol^{-1} and incorporation values of 1.9 mol % and 0.68 mol %, respectively (Table 2, entries 5 and 7). The higher DAE incorporation can be attributed to the doubled concentration of terminal double bonds in diallyl ether. Also, in this case, complex **7c**, which bears a bulkier substituent on the nitrogen atom, generates a copolymer with higher molecular weight, albeit with lower allyl ether incorporation (Table 2, entries 6 and 8). NMR analysis revealed that linear structure **I**, 3,4-disubstituted tetrahydrofuran structure **II**, and 3,5-disubstituted tetrahydropyran structure **III** were included in the ethylene/DAE copolymer, whereas 3,6-disubstituted oxepane structure **IV** was not observed.[26] The ratio of structures **I**/**II**/**III** was approximately 1:1:2 for entries 5 and 6. Based on the observed copolymers structures, the insertion mechanism of DAE is explored in Scheme 2. There are two possible insertion modes of DAE: 1) 2,1-insertion to form β-alkoxy intermediate **A**, and 2) 1,2-insertion to form γ-alkoxy intermediate **B**. In both cases, ethylene incorporation without cyclization can form structure **I**, which has one terminal



Scheme 2. Mechanism for the incorporation of diallyl ether.

double bond. From intermediate **A**, *exo*-cyclization forms 5-membered ring structure **D** and *endo*-cyclization forms 6-membered ring structure **E**, leading to structures **II** and **III**, respectively. The former pathway is much more probable because, according to the literature, [2-(allyloxy)ethyl] nickel species predominantly undergo *exo*-cyclization.[29] The formation of **III** results from the 1,2-insertion of DAE to form intermediate **B** and subsequent *exo*-cyclization to generate intermediate **G**. *Endo*-cyclization to form 7-membered ring structure **H** was excluded by the absence of structure **IV** in the copolymer.

Other comonomers, such as methyl acrylate (Table 2, MA; entry 9) and acrylonitrile (entry 10), suppressed the polymerization reaction. In a recent study on bisphosphine monoxide palladium complexes, we found that the copolymerization of ethylene and MA is significantly retarded after 1,2-insertion of MA.[5b] Considering that in the Pd/IzQO system, 1,2-selective MA insertion was suggested,[23] we propose that 1,2-insertion of MA to form a five-membered chelation ring might have occurred, thereby suppressing coordination to the nickel center.

In summary, a series of phenyl(triethylphosphine)nickel complexes bearing imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) ligands (**7 a–c**) were synthesized and characterized. The Ni/IzQO complexes can initiate ethylene polymerization at 50–100 °C without any cocatalyst. Activation by $[\mathrm{Ni(cod)_2}]$ increased the catalytic activity up to $1.2\times10^3\ \mathrm{kg\,mol^{-1}\,h^{-1}}$, and lowered the reaction temperature, thereby increasing the M_n of polyethylene up to $84\ \mathrm{kg\,mol^{-1}}$. In addition, the Ni/IzQO system can catalyze the copolymerization of ethylene with allyl acetate and allyl ethers. To the best of our knowledge, this is the first reported nickel catalyst that can form copolymers of ethylene and allyl acetate with M_n greater than $4.5\ \mathrm{kg\,mol^{-1}}$, and is the first reported nickel-catalyzed ethylene/allyl ether copolymerization. Further expansion of the substrate scope for the Ni/IzQO system, including propylene polymerization, is currently underway in our laboratory.

Acknowledgements

This work was supported by CREST, JST. A part of this work was conducted in Research Hub for Advanced Nano Characterization, The University of Tokyo, supported by MEXT, Japan. W-J. T. is grateful for the financial support from Shanghai Institute of Organic Chemistry, Zhejiang Medicine, and Pharmaron for a joint postdoctoral fellowship. R.N. acknowledges the Japan Society for the Promotion of Science (JSPS) for a Research Fellowship for Young Scientists.

Keywords: ethylene · IzQO · nickel · polar monomers · polymerization

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2835–2839
Angew. Chem. **2016**, *128*, 2885–2889

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Received: October 29, 2015