# Copolymerization of Propylene and Polar Monomers Using Pd/IzQO Catalysts

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**S** *Supporting Information*

**ABSTRACT:** Palladium catalysts bearing imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) ligands polymerize $\alpha$-olefins while incorporating polar monomers. The steric environment provided by N-heterocyclic-carbene (NHC) enables regioselective insertion of $\alpha$-olefins and polar monomers, yielding polypropylene, propylene/allyl carboxylate copolymers, and propylene/methyl acrylate copolymer. Known polymerization catalysts bearing NHC-based ligands decompose rapidly, whereas the present catalyst is durable because of structural confinement, wherein the NHC-plane is coplanar to the metal square plane. The present catalyst system enables facile access to a new class of functionalized polyolefins and helps conceive a new fundamental principle for designing NHC-based ligands.

Introduction of polar functional groups into polyolefins, namely polyethylene and polypropylene, has been pursued to improve the material properties in the resulting "functional polyolefins".[1,2] Direct preparation of "functional polyethylene" was achieved by incorporating polar monomers either by radical copolymerization or by the recently developed coordination–insertion copolymerization.[2] The synthetic approach to achieve "functional polypropylene" has been limited to postmodification techniques. However, the postmodification processes industrialized at present have certain limitations such as chain-shortening, limited main-chain functionalization, and a narrow functional group scope, thereby restricting the application of "functional polypropylene".[3] In spite of the successful synthesis of "functional polyethylene" by coordination–insertion copolymerization, the propylene/polar monomer copolymerization remains a formidable challenge. Early transition-metal catalysts used in industrial polypropylene production are heavily poisoned by heteroatoms, which only allows for the indirect introduction of polar functional groups by either protection/deprotection of the polar groups or postconversion of less-polar but reactive intermediates.[4] On the other hand, late-transition-metal catalysts that are tolerable to heteroatoms suffer from contamination of regiodefects such as head-to-head/tail-to-tail defects and a linear structure during propylene polymerization (Scheme 1a). The reported methods for regioregular propylene polymerization with group-10-metal catalysts require very low-temperature conditions (i.e., much below room temperature),[5] which cannot provide copolymers with polar monomers.[2d,6]

**Scheme 1. Typical Structural Errors during Polypropylene Formation by Late-Transition-Metal Catalysts and the Mechanistic Pathways for the Formation of Structural Errors**
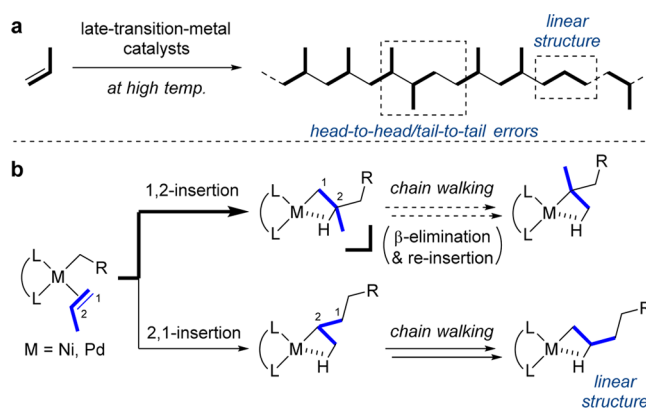


From a mechanistic viewpoint, the formation of structural irregularities is attributed to (i) the poor regioselectivity of propylene insertion and (ii) $\beta$-hydride elimination and subsequent isomerization called chain-walking (Scheme 1b).[7] There are two insertion modes for propylene: 1,2-insertion, forming the primary chain-end (upper); and 2,1-insertion, forming the secondary chain-end (lower). After both insertion modes, chain-walking, a common side reaction observed with late-transition-metal catalysts, may result in structural errors such as the formation of a linear structure, unless $\beta$-hydride elimination is effectively suppressed. In order to avoid head-to-head/tail-to-tail defects, the insertion mode needs to be regularly controlled to be either 1,2- or 2,1-insertion. The more desirable of the two insertion modes is the 1,2-mode, as chain-walking is less likely in this case because of the postinsertion kinetic and thermodynamic instability of the tertiary chain-end in the isomerized product. On the other hand, the facile isomerization from the secondary chain-end to the primary after 2,1-insertion increases the likelihood of chain-walking. Therefore, the deduced mechanistic keys to avoid regiodefect formation are (i) suppression of the $\beta$-hydride elimination that leads to chain-walking and (ii) 1,2-selective propylene insertion. Here, we describe our design of palladium catalysts bearing novel tethered N-heterocyclic carbene (NHC) ligands that satisfy the above two premises for the successful copolymerization of propylene with polar monomers.
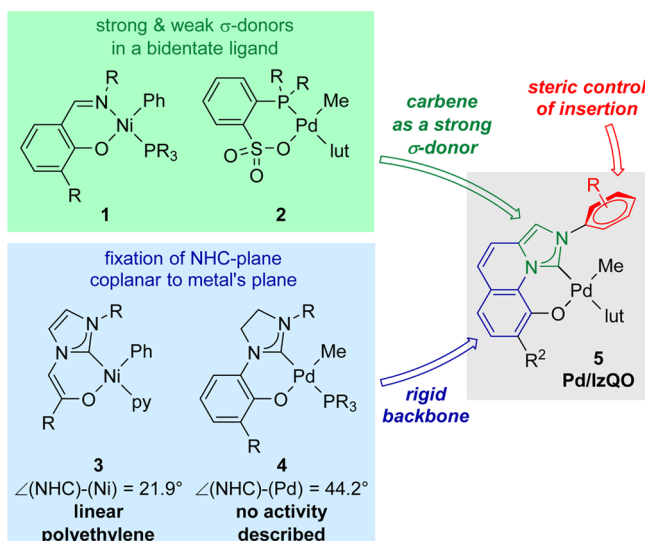
**Figure 1.** Design of imidazo[1,5-*a*]quinolin-9-olate-1-ylidene ligands **5**, based on complexes **1**−**4**.

**Scheme 2. Synthetic Scheme of Carbene Precursors 6a−c and Their Palladium Complexes 5a−c[a]**



[a]Dip, 2,6-diisopropylphenyl; Mes, 2,4,6-trimethylphenyl; lut, 2,6-lutidine.

Three design concepts for imidazo[1,5-*a*]quinolin-9-ylidene (IzQO) ligands are highlighted in the green, red, and blue parts in Figure 1. To suppress $\beta$-hydride elimination, the combination of a strong and weak $\sigma$-donor motif in a bidentate ligand has proved effective, as in nickel/salicylaldiminate **1** and palladium/phosphine-sulfonate **2**; both the catalysts successfully incorporated polar monomers into linear polyethylene (Figure 1).[8−11] We employed NHCs as the strong donor motif in bidentate ligands, expecting their strong $\sigma$-donating ability to enhance the electronic asymmetry in the bidentate ligands (Figure 1, green part).[12] Moreover, the optimal orientation of modifiable substituents on the nitrogen atom enables a congested environment appropriate for the sterically less demanding 1,2-insertion of olefins (Figure 1, red part). Many group-10-metal complexes bearing NHC-based ligands were subjected to olefin polymerization, but most candidates showed poor activity for ethylene oligomerization.[13,14] The commonly accepted decomposition pathway of the catalysts is irreversible reductive elimination, forming imidazolium salts from metal hydride species, wherein the hydride attacks the vacant p-orbital of carbenes.[15] A noteworthy exception in the literature is nickel/NHC-enolate **3** reported by Waymouth, which can form linear polyethylene and low-molecular-weight polypropylene with a short lifetime.[14c−e] To devise methods for further enhancing the catalyst durability, structural comparisons were made with complex **4** bearing the electronically similar NHC-phenolate ligand, which is inactive for polymerization.[14a] While the NHC-moiety of **3** is nearly coplanar to the metal coordination square, with a mean dihedral angle of 21.9°, the NHC-moiety of **4** is twisted from the metal plane, with a mean dihedral angle of 44.2° (see Supporting Information Section IV for the definition of mean dihedral angle). The differences in the catalytic activities and crystal structures between **3** and **4** led us to postulate that the NHC-plane and metal plane should always be coplanar, so that overlap between the vacant p-orbitals of carbene and the cis-metal-hydride is minimized, and thus catalyst decomposition via reductive elimination is retarded. This idea is reflected in the rigid skeleton of palladium/IzQO complex **5** (Figure 1, blue part), in which the NHC-plane is fixed onto the palladium square plane.

The synthesis of the ligand precursors **6a−c** and their palladium complexes **5a−c** is summarized in Scheme 2. The
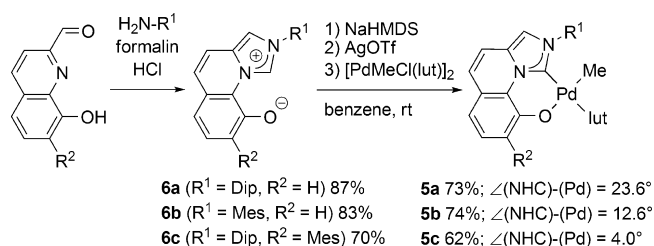
imidazo[1,5-*a*]quinolin-9-olate skeleton was readily prepared by the condensation of 8-hydroxyquinoline-2-carbaldehyde, anilines, and formaldehyde.[16] After deprotonation by NaHMDS and subsequent carbene transfer to silver(I), trans-metalation using [(2,6-lutidine)PdMeCl]$_2$ afforded the corresponding (IzQO)PdMe(2,6-lutidine) complexes **5a−c** in good yields. Complexes **5a−c** were structurally characterized by X-ray crystallography. The mean dihedral angles between the NHC-plane and the palladium square plane in **5a−c** were found to be small at 23.6°, 12.6°, and 4.0°.

Palladium/IzQO complexes were employed for the homopolymerization of ethylene, propylene, and 1-butene (Table 1). Despite the reported thermal instability of NHC-based complexes, **5a** exhibited the best activity for linear polyethylene production at 100 °C (entries 1−3). The high molecular weight of polyethylene formed by the use of **5a** is noteworthy, since palladium catalysts yielding linear polyethylene with $M_n > 50,000$ are still rare.[17] Compound **5b** bearing a mesityl substituent ($R^1$) produced lower-molecular-weight polyethylene and showed poor catalytic activity (entry 4). Compound **5c** bearing a bulky substituent as $R^2$ exhibited augmented activity and afforded polyethylene with moderate molecular weight (entry 5). The high molecular weight of polyethylene obtained when using **5a** encouraged us to investigate propylene polymerization by **5a** (entries 6−8). We found that **5a** could catalyze propylene polymerization at 80−120 °C. Quantitative ^{13}C NMR analysis revealed that the regiodefects in the obtained polypropylenes were <1.5 mol %. While the effect of $R^1$ and $R^2$ on propylene polymerization was similar to that on ethylene polymerization (entries 2, 4, 5, 7, 9, and 10), **5b** formed polypropylene with smaller molecular weight and a greater amount of linear structures than the products in the other cases (entry 9). DFT calculation for propylene insertion into a Pd-isobutyl bond suggested that both **5a** and **5b** favored 1,2-insertion of propylene over 2,1-insertion, with $\Delta\Delta G^{\ddagger}$ of 3.6 and 1.8 kcal/mol, respectively. This result is in accord with the fact that a greater proportion of regiodefects is seen in polypropylene formed by **5b** than in polypropylene formed by **5a** (Supporting Information Section VII). Consequently, **5a** and **5c** bearing Dip as $R^1$ were found to be effective for the polymerization of 1-butene, yielding poly(1-butene)s with moderate molecular weights (entries 11 and 12).

The scope of polar monomers employable with Pd/IzQO catalysts was screened by ethylene copolymerization using **5a** (Table 2, entries 1−8). The selective 1,2-insertion of olefins by **5a** was deemed appropriate for the incorporation of allyl monomers, including allyl acetate (AAc), allyl pivalate (APiv), and allyl chloride (AC) (entries 1−3), as the functional groups should be on the $\gamma$-carbon after 1,2-insertion. Among the vinyl

**Table 1. Homopolymerization of Ethylene, Propylene and 1-Butene by Catalysts 5a−c**[a]

| entry | cat. (μmol) | olefin | temp (°C) | time (h) | activity (kg mol$^{-1}$ h$^{-1}$) | $M_n$ ($10^3$) | $M_w/M_n$ | regio defects[b] (mol %) |
|---|---|---|---|---|---|---|---|---|
| 1 | **5a** (1.0) | ethylene (4.0 MPa) | 80 | 1.0 | 33 | 26 (61) | 2.1 | − |
| 2 | **5a** (1.0) | | 100 | 1.0 | 691 | 76 (180) | 2.4 | − |
| 3 | **5a** (1.0) | | 120 | 1.0 | 451 | 80 (189) | 2.0 | − |
| 4 | **5b** (1.0) | | 100 | 2.0 | 55 | 19 (43) | 3.3 | − |
| 5 | **5c** (1.0) | | 100 | 1.0 | 1310 | 51 (121) | 2.9 | − |
| 6 | **5a** (2.0) | propylene (10.0 g) | 80 | 3.0 | 10 | 16 (25) | 2.0 | 0.4 |
| 7 | **5a** (2.0) | | 100 | 3.0 | 34 | 16 (26) | 2.2 | 1.2 |
| 8 | **5a** (2.0) | | 120 | 3.0 | 23 | 11 (17) | 2.9 | 1.5 |
| 9 | **5b** (2.0) | | 100 | 3.0 | 3.6 | 2.1 (2.9) | 1.9 | 2.1 |
| 10 | **5c** (2.0) | | 100 | 3.0 | 52 | 18 (29) | 2.5 | 1.4 |
| 11 | **5a** (5.0) | 1-butene (5.0 g) | 100 | 3.0 | 9.0 | (24) | 2.1 | <0.1 |
| 12 | **5c** (5.0) | | 100 | 3.0 | 6.0 | (19/1.3)[c] | 1.8/1.2[c] | n.d.[c] |

[a]A mixture of catalyst and olefin in 20 mL of toluene was stirred under the conditions mentioned in Table 1. [b]Determined by quantitative $^{13}$C NMR analysis. [c]Bimodal distribution. The peak area ratio of the former peak with $M_n$ of 19,000 and the latter peak with $M_n$ of 1,300 was 6.5/1. The amount of regiodefects could not be determined due to the contamination of oligomers.

**Table 2. Copolymerization of Ethylene or Propylene with Polar Monomers by Catalysts 5a and 5c**[a]



| entry | catalyst (R$^1$-R$^2$) | olefin | polar monomer (mL) | temp (°C) | time (h) | activity (kg mol$^{-1}$ h$^{-1}$) | $M_n$[b] (/$10^3$) | $M_w/M_n$[b] | incorp[c] (mol %) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **5a** (Dip-H) | ethylene (4.0 MPa) | AAc (1.0) | 100 | 3.0 | 4.5 | 7.4 (17) | 2.5 | 1.4 |
| 2 | **5a** (Dip-H) | | APiv (2.0) | 100 | 3.0 | 5.2 | 5.0 (11) | 5.6 | 1.1 |
| 3 | **5a** (Dip-H) | | AC (0.40) | 100 | 3.0 | 1.3 | 4.0 (9.0) | 2.1 | 0.5 |
| 4 | **5a** (Dip-H) | | MA (0.20) | 100 | 3.0 | 10.6 | 17 (39) | 2.0 | 0.8 |
| 5 | **5a** (Dip-H) | | TBA (0.40) | 100 | 3.0 | 7.2 | 2.3 (5.2) | 3.2 | 0.7 |
| 6 | **5a** (Dip-H) | | AN (0.20) | 120 | 48 | < 0.01 | - | - | - |
| 7 | **5a** (Dip-H) | | VAc (1.0) | 100 | 3.0 | 6.3 | 11 (26) | 2.5 | < 0.1 |
| 8 | **5a** (Dip-H) | | BVE (1.0) | 100 | 3.0 | 10.8 | 23 (55) | 2.7 | < 0.1 |
| 9 | **5a** (Dip-H) | propylene (10.0 g) | AAc (0.10) | 100 | 6.0 | 1.3 | 3.9 (5.8) | 2.2 | 2.0 |
| 10 | **5c** (Dip-Mes) | | AAc (0.10) | 100 | 6.0 | 2.8 | 11 (16) | 2.3 | 0.9 |
| 11 | **5a** (Dip-H) | | APiv (0.10) | 100 | 6.0 | 2.0 | 7.7 (12) | 2.4 | 1.2 |
| 12 | **5c** (Dip-Mes) | | APiv (0.10) | 100 | 6.0 | 5.4 | 13 (20) | 2.5 | 0.5 |
| 13 | **5a** (Dip-H) | | MA (0.010) | 100 | 6.0 | 0.69 | 3.0 (4.4) | 2.2 | 1.5 |
| 14 | **5a** (Dip-H) | | MA (0.005) | 100 | 6.0 | 2.0 | 5.4 (8.0) | 2.8 | 0.6 |
| 15 | **5c** (Dip-Mes) | | MA (0.005) | 100 | 6.0 | 0.74 | 3.0 (4.4) | 3.0 | 1.1 |

[a]A mixture of catalyst (10 μmol), olefin, and polar monomer in toluene was stirred under the conditions mentioned in Table 2. The total volume of polar monomers and toluene was set to 20 mL. MA, methyl acrylate; TBA, *tert*-butyl acrylate; AN, acrylonitrile; VAc, vinyl acetate; BVE, butyl vinyl ether; AAc, allyl acetate; APiv, allyl pivalate; AC, allyl chloride. [b]By size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. Molecular weights before universal calibration are shown in parentheses. [c]Determined by quantitative $^{13}$C NMR or $^1$H NMR analysis.

monomers commonly copolymerized with ethylene, methyl acrylate (MA), and *tert*-butyl acrylate (TBA) were successfully incorporated by **5a** into linear polyethylene (entries 4 and 5). On the other hand, when using acrylonitrile (AN), the activity of **5a** was nearly quenched (entry 6). The use of butyl vinyl ether (BVE) or vinyl acetate (VA) with **5a** resulted in the formation of lower-molecular-weight polyethylene without functional groups (entries 7 and 8), suggesting 1,2-selective insertion of polar monomers and subsequent β-alkoxide or β-acetate eliminations. Based on the above-mentioned results of ethylene/polar monomer copolymerization, AAc, APiv, and MA were chosen as comonomers for copolymerization with propylene.

Finally, copolymerization of propylene with polar monomers was accomplished by using **5a** and **5c** (Table 2, entries 9−15). In order to achieve reasonable activity for ~1 mol % incorporation of polar monomers, we decreased the concentration of polar

monomers to 1/10−1/20 based on the homopolymerization activities of ethylene and propylene shown in Table 1. AAc and APiv were successfully incorporated into polypropylene by both **5a** and **5c** (entries 9−12). The catalytic activities in propylene/AAc and propylene/APiv copolymerization were on the same order as those for ethylene/AAc and ethylene/APiv copolymerization, suggesting that copolymerization activity is not dominated by the homopolymerization activities of the olefins. In the presence of MA, **5a** afforded propylene/MA copolymer with 1.5 mol % incorporation of MA (entry 13). When the concentration of MA was reduced by 50% (entry 14), the activity and molecular weight increased almost 2-fold as compared to those in entry 13, while the incorporation ratio was reduced. On the other hand, when using the sterically congested **5c** (entry 15), a similar result to entry 13 was observed. Quantitative $^{13}$C NMR analysis of the copolymers suggested that the copolymer

mostly comprised 1,2-propylene structures and that polar monomers were incorporated majorly into the main chain of polypropylene with same direction as propylene (See Supporting Information Sections VI–III for the details).[18]

In conclusion, the new palladium complexes bearing imidazo-[1,5-*a*]quinolin-9-olate-1-ylidene ligands can act as ubiquitous catalysts for olefin polymerization, including *α*-olefin homo-polymerization and the unprecedented propylene/polar-mono-mer copolymerization. The Pd/IzQO system represents one of the few successful demonstrations of NHC-based ligands for olefin polymerization, highlighting the significance of our design focusing on structural confinement of the NHC-plane onto metal plane. This principle can be further extended to broaden the applicability of NHC-based ligands for other catalytic applications. The new family of "functional poly(*α*-olefin)s" synthesized here would pave the way for the production of polyolefin composites with polar materials. For industrial applications, there still remain many challenges. First, substantial advancement in catalytic activity is indispensable. Second, the "functional polypropylenes" prepared here remain atactic and contain only up to 2.0 mol % of functional groups. Further tacticity control is essential to endow the product with the excellent material properties of polypropylene such as good mechanical strength and heat resistance, which only appears when the highest control of stereoregularity is achieved. Although ~1% incorporation of polar functional group was reported to be sufficient to improve affinity to certain polar materials in the previous studies on postfunctionalized polypropylene,[19] method which can utilize various polar monomers and tolerate greater amount of polar monomer incorporation will greatly benefit to broaden applications of functional polypropylene. Efforts to address these issues are underway in our group.

## ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06948.

> Experimental procedures, characterization of palladium com- pounds and polymers, crystallographic data for **5a–c**, and data of theoretical calculation (PDF)
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### Notes
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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