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# Fluorinated α-Diimine Nickel Mediated Ethylene (Co)Polymerization

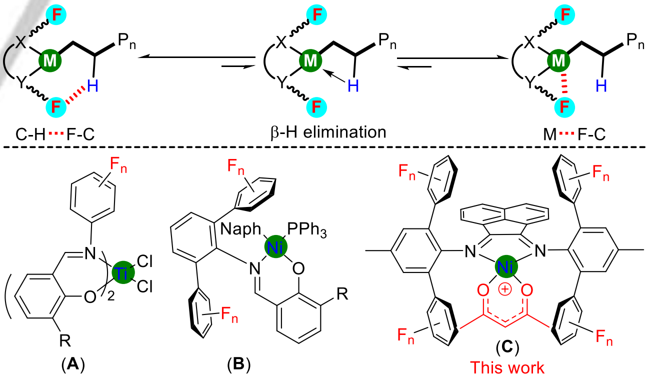
Xiaoqiang Hu,[a,b] Yixin Zhang,[a] Baixiang Li,[a] Zhongbao Jian*[a,b]

**Abstract:** Fluorine substituents in transition metal catalysts are of significantly great importance in olefin polymerization catalysis; however, the comprehensive effect of fluorine substituents is elusive in seminal late transition metal α-diimine catalytic system. In this contribution, fluorine substituents at various positions (*ortho*-, *meta*-, and *para*-F) and with different numbers ($F_n$; n = 0, 1, 2, 3, 5) were installed into the well-defined *N*-terphenyl amine and thus were studied for the first time in the nickel α-diimine promoted ethylene polymerization and copolymerization with polar monomers. The position of the fluorine substituent was particularly crucial in these polymerization reactions in terms of catalytic activity, polymer molecular weight, branching density, and incorporation of polar monomer, and thus a picture on the fluorine effect was given. As a notable result, the *ortho*-F substituted α-diimine nickel catalyst produced highly linear polyethylenes with an extremely high molecular weight ($M_w$ = 8,703 kDa) and a significantly low degree of branching of 1.4/1000 C; however, the *meta*-F and/or *para*-F substituted α-diimine nickel catalysts generated highly branched (up to 80.2/1000 C) polyethylenes with significantly low molecular weights ($M_w$ = 20-50 kDa).

## Introduction

The role of fluorine substituents is of great importance in organic products, homogeneous catalysis, and olefin polymerization catalysis as well. An event of β-H elimination that leads to chain transfer reaction is necessarily suppressed for obtaining high molecular weight polymers in olefin polymerization.[1-3] For this purpose, advanced techniques[4] including steric and electronic regulation of ligands,[5-9] redox strategy,[10-13] secondary interaction,[14,15] and bimetallic synergistic effect[16-20] have been extensively utilized in the design of early- and late-transition-metal catalysts. Notably, fluorine substituents mainly the *ortho*-F substitution in olefin polymerization catalysts are also a powerful tool for inhibiting chain transfer reaction because of the weakly donating nature.[21] The prominent case is that phenoxy-imine or enolatoimine titanium catalysts bearing fluorine substituents feature a living nature for polymerization of ethylene and propylene (Scheme 1A).[22-27] A C-H···F-C interaction between the *ortho*-F substitution with the β-H atoms of the growing chain is proposed to suppress chain transfer process (Scheme 1).

Strikingly, late-transition nickel catalysts more easily suffer from a more pronounced β-H elimination reaction, resulting in chain transfer and also the seminal chain walking in ethylene polymerization.[28-66] Fluorine substituents in these catalysts is also effective in tuning elementary reaction pathways, likewise. Phenoxy-imine nickel catalysts bearing fluorine (F) substituents or fluorocarbon ($C_nF_{2n+1}$) substituents have been thoroughly studied in ethylene polymerization (Scheme 1B).[67-74] The effect of fluorine substituents on thermal stability and activity of catalyst, and molecular weight and branching density of polymer is observed. In contrast, study on the influence of fluorine substituents in the classic Brookhart α-diimine nickel catalyst is particularly rare, although it is definitely important to enrich the milestone α-diimine species.[75] A notable example is that installing *ortho*-F substituents into a cyclophane-based α-diimine nickel catalyst leads to substantial differences in catalytic behavior and polymer property in ethylene polymerization.[76] A unique M···F interaction between the *ortho*-F substitution with the active metal center is elucidated to stabilize the highly reactive 14e⁻ alkyl intermediate (Scheme 1), thereby suppressing the β-H elimination reaction. The result is indicative of the important effect of fluorine substituents; however, comprehensive study on the fluorinated effect is inhibited by unavailable catalysts based on this special cyclophane α-diimine framework, and thus is elusive thus far.



**Scheme 1.** Proposed roles of fluorine substituents in catalytic olefin polymerization (Top) and the related catalysts applied (Bottom).

We are interested in terphenyl-based α-diimine nickel catalysts for olefin (co)polymerizations.[65] In this contribution, we now show that, using a feasible *N*-terphenyl framework, fluorine substituents at various positions and with different numbers are installed into α-diimine nickel catalysts for ethylene polymerization and copolymerization with polar monomers (Scheme 1C). This for the first time enables an investigation on the effect of *ortho*-, *meta*-, and *para*-F substituents in the α-diimine system with regard to

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Supporting information for this article is given via a link at the end of the document. General procedures, and characterization and analysis data (NMR, GPC, DSC, and IR) for anilines, ligands, complexes (CCDC Nos.: 2017269 (**Ni-1F**), 2017273 (**Ni-2F**), and 2017274 (**Ni-5F**); These data are provided free of charge by Cambridge Crystallographic Data Centre), polyethylenes, and copolymers (108 pages).

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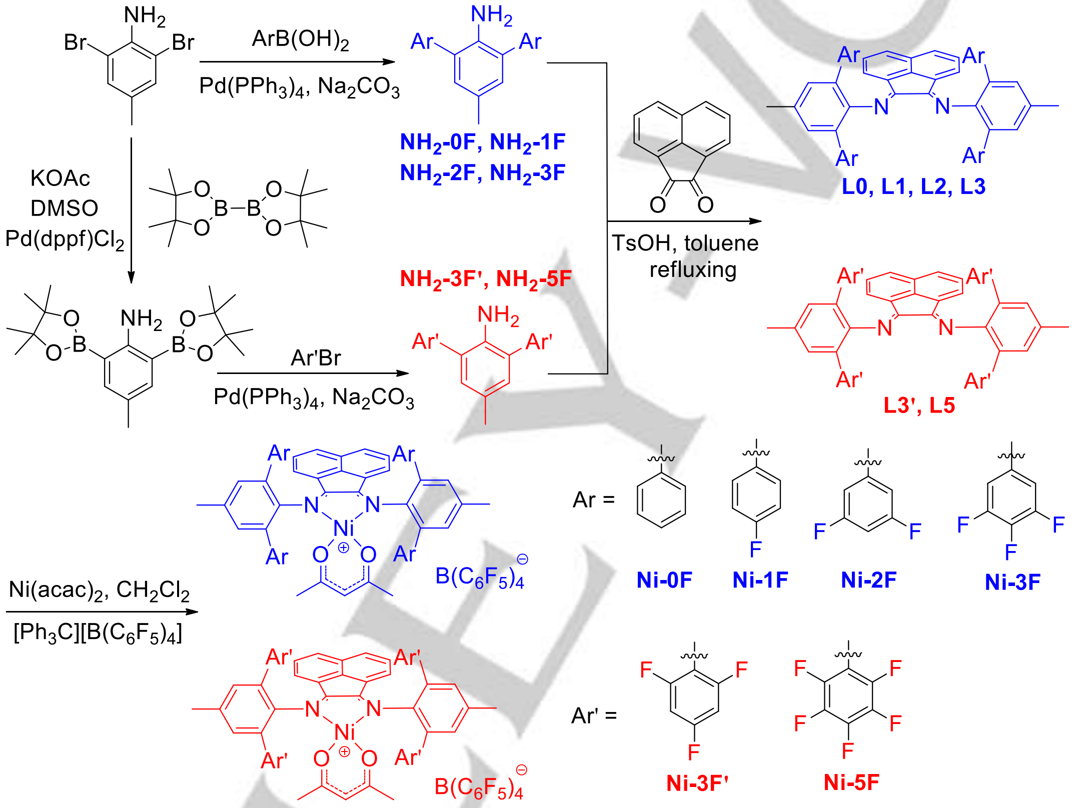
catalytic activity, polymer molecular weight and branching density, and incorporation of polar monomer.

## Results and Discussion

**Nickel catalysts design**. To access the fluorinated α-diimine ligands and the corresponding α-diimine nickel catalysts, two completely different methods were utilized to synthesize a series of fluorine-containing anilines, due to the low nucleophilicity of the aryl groups that contain *ortho*-fluorine atoms (Scheme 2).[77] Rigid *N*-terphenylamines ($NH_2$-0F, $NH_2$-1F, $NH_2$-2F, and $NH_2$-3F) without *ortho*-fluorine atoms could be easily synthesized through the classic Suzuki coupling reaction of 2,6-dibromo-4-methylaniline with the corresponding arylboronic acids. However, for *N*-terphenylamines ($NH_2$-3F' and $NH_2$-5F) containing *ortho*-fluorine atoms, it is essential to first borylation of 2,6-dibromo-4-methylaniline and then Suzuki coupling with the corresponding aryl bromide compounds. Subsequently, a series of fluorinated α-diimine ligands could be prepared in excellent yields by *p*-toluenesulfonic acid catalyzed condensation reaction of acenaphthoquinone with 2.05 equiv. of the *N*-terphenylamine in toluene for several days at 120 °C. All of these α-diimine ligands were characterized by elemental analysis and $^1H/^{13}C$ NMR spectroscopy (for details, see Supporting Information).



**Scheme 2.** Synthetic routes of the fluorinated α-diimine ligands and the related Ni(II) catalysts.

**Figure 1.** Molecular structures of the cation part of **Ni-1F, Ni-2F** and **Ni-5F** drawn with 30% probability ellipsoids. Hydrogen atoms and borate anion are omitted for clarity. **Ni-1F**: selected bond lengths (Å): Ni1-O1 1.812(2), Ni1-O2 1.817(2), Ni1-N1 1.915(2), Ni1-N2 1.921(2); selected bond angles (°): O2-Ni1-N1 175.97(8), O2-Ni1-N2 91.23(8), O1-Ni1-O2 96.16(7), O1-Ni1-N1 87.87(8), O1-Ni1-N2 172.28(8), N1-Ni1-N2 84.76(8). **Ni-2F**: selected bond lengths (Å): Ni1-O1 1.812(4), Ni1-O2 1.797(5), Ni1-N1 1.896(5), Ni1-N2 1.883(5); selected bond angles (°): O2-Ni1-O1 95.4(2), O2-Ni1-N2 89.2(2), O1-Ni1-N2 175.3(2), O2-Ni1-N1 175.1(2), O1-Ni1-N1 89.3(2), N2-Ni1-N1 86.1(2). **Ni-5F**: selected bond lengths (Å): Ni1-O1 1.809(2), Ni1-O2 1.807(2), Ni1-N1 1.915(2), Ni1-N2 1.925(2); selected bond angles (°): O2-Ni1-O1 96.64(9), O2-Ni1-N2 89.53(9), O2-Ni1-N1 173.13(9), O1-Ni1-N2 173.33(10), O1-Ni1-N1 89.40(9), N1-Ni1-N2 84.59(9).

The corresponding α-diimine nickel complexes **Ni-0F**, **Ni-1F**, **Ni-2F**, **Ni-3F**, **Ni-3F'**, and **Ni-5F** could be synthesized by a typical reaction of α-diimine ligand with 1 equiv. of Ni(acac)$_2$ and 1 equiv. of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. The pure nickel precatalysts could be separated from the mixture by simply washing with diethyl ether and *n*-hexane, which were fully identified by elemental analysis and $^1$H/$^{13}$C/$^{19}$F NMR spectroscopy (for details, see SI). Note that the usual dibromo nickel complexes were unavailable when reacting ligands **L2~L5** with NiBr$_2$(DME). In particular, single crystals of **Ni-1F**, **Ni-2F**, and **Ni-5F** that are suitable for X-ray diffraction analysis were obtained by a solvent diffusion (dichloromethane/*n*-hexane) method and their molecular structures were verified in Figure 1. The acac-based Ni(II) centers in **Ni-1F**, **Ni-2F**, and **Ni-5F** sited in a square planar coordination sphere defined by N1, N2, O1, and O2, which is in contrast to the typical tetrahedral geometry of dibromo Ni(II) complexes. In **Ni-5F**, the closest distance between the *ortho*-F atom and the Ni(II) center was 3.238 Å, which is shorter than the sum of the van der Waals radii of the Ni and F atoms (3.31 Å). This potential intramolecular interaction (Ni···F interaction) might compete with ethylene coordination and β-H elimination, thus affecting catalytic properties. Note that there is no correlation between the number of fluorine atoms on the ligand and the Ni-N bond lengths.

**Effect of fluorine substituents on ethylene polymerization.** *In situ* activated with 500 equiv. of AlEt$_2$Cl (screening of alkyl aluminum reagents including MAO, MMAO, AlEt$_2$Cl, TiBA, TMA, and EASC in ethylene polymerization could be found in Table S1 of Supporting Information), all six α-diimine Ni(II) catalysts **Ni-0F**~**Ni-5F** showed high activities (10$^6$~10$^7$ g mol$^{-1}$ h$^{-1}$) in ethylene polymerization (Table 1). Overall, catalytic activities dropped rationally with the increase of temperature from 30 °C to 90 °C; however, at the harsh temperature of 120 °C, catalytic activity still maintained on a high level of 3.3 × 10$^6$ g mol$^{-1}$ h$^{-1}$ (Table 1, entry 19). Furthermore, as anticipated, the molecular weight of the generated polyethylenes decreased with elevating temperature, which is attributed to a faster chain transfer rate with increasing temperature. In addition, branching densities of these polyethylenes obtained could be varied in a wide range (1.2~80.2/1000C). The results revealed that branching density is related to not only the structure of catalysts but also the polymerization temperature. The elevated temperature resulted in increasing of branching density obviously, indicating that branching density can be tuned by varying temperature. Also, the polymer melting point fell dramatically with the increase of branching density.

The effect of fluorine substituents at different positions with various numbers in α-diimine Ni(II) catalysts was studied in detail in ethylene polymerization (Figure 2). In comparison with the non-fluorinated catalyst **Ni-0F**, the catalyst **Ni-1F** containing four *para*-F atoms produced polyethylenes with slightly higher activities. Branching densities were higher, but polymer molecular weights ($M_w$) dropped (Table 1, entries 1-3 vs. 4-6). In terms of the catalyst **Ni-2F** that contains eight *meta*-F atoms, the polymerization reaction not only exhibited slightly lower activities but also lower

**Table 1.** Ethylene polymerization with fluorinated nickel catalysts.[a]

| Entry | Cat. | $T$ (°C) | $t$ (min) | Yield (g) | Act. (10$^7$)[b] | $M_w$ (10$^4$)[c] | $M_w$/$M_n$[c] | brs[d] | $T_m$[e] (°C) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **Ni-0F** | 30 | 10 | 5.74 | 3.44 | 15.0 | 2.57 | 26.7 | 112.3 |
| 2 | **Ni-0F** | 60 | 10 | 4.61 | 2.77 | 5.5 | 2.11 | 36.5 | 95.1 |
| 3 | **Ni-0F** | 90 | 10 | 3.05 | 1.83 | 3.2 | 1.84 | 45.0 | 72.0 |
| 4 | **Ni-1F** | 30 | 10 | 6.01 | 3.61 | 3.7 | 2.14 | 44.3 | 97.6 |
| 5 | **Ni-1F** | 60 | 10 | 5.58 | 3.35 | 2.7 | 1.82 | 58.7 | 71.4 |
| 6 | **Ni-1F** | 90 | 10 | 3.17 | 1.90 | 2.0 | 1.95 | 63.4 | 53.9 |
| 7 | **Ni-2F** | 30 | 10 | 5.32 | 3.19 | 4.7 | 2.00 | 68.2 | 62.8 |
| 8 | **Ni-2F** | 60 | 10 | 4.01 | 2.41 | 3.5 | 1.95 | 76.1 | 37.8 |
| 9 | **Ni-2F** | 90 | 10 | 2.55 | 1.53 | 2.5 | 1.85 | 80.2 | - |
| 10 | **Ni-3F** | 30 | 10 | 5.20 | 3.12 | 5.0 | 1.87 | 66.6 | 68.7 |
| 11 | **Ni-3F** | 60 | 10 | 1.82 | 1.09 | 4.0 | 1.88 | 76.5 | 42.6 |
| 12 | **Ni-3F** | 90 | 10 | 1.66 | 1.00 | 2.8 | 1.95 | 80.1 | - |
| 13 | **Ni-3F'** | 0 | 10 | 1.76 | 1.06 | 254.2 | 1.49 | 2.6 | 130.1 |
| 14 | **Ni-3F'** | 30 | 10 | 1.30 | 0.78 | 66.4 | 1.40 | 6.3 | 120.1 |
| 15 | **Ni-3F'** | 60 | 10 | 0.92 | 0.55 | 48.3 | 1.44 | 10.7 | 114.0 |
| 16 | **Ni-3F'** | 60 | 20 | 1.58 | 0.47 | 121.9 | 1.32 | 12.0 | 112.3 |
| 17 | **Ni-3F'** | 60 | 40 | 3.04 | 0.46 | 172.9 | 1.39 | 11.7 | 111.0 |
| 18 | **Ni-3F'** | 90 | 10 | 0.81 | 0.49 | 34.4 | 1.46 | 14.7 | 105.3 |
| 19 | **Ni-3F'** | 120 | 10 | 0.55 | 0.33 | 26.9 | 1.61 | 17.1 | 99.3 |
| 20 | **Ni-3F'** | 0 | 20 | 3.61 | 1.08 | 446.9 | 1.58 | 2.8 | 128.2 |
| 21 | **Ni-3F'** | 0 | 30 | 5.15 | 1.03 | 620.7 | 1.46 | 4.0 | 126.4 |
| 22[f] | **Ni-3F'** | 0 | 60 | 10.12 | 1.01 | 821.6 | 1.63 | 4.2 | 125.4 |
| 23[f] | **Ni-3F'** | 0 | 120 | 24.45 | 1.22 | [h]- | [h]- | 5.2 | 124.5 |
| 24[g] | **Ni-3F'** | 0 | 30 | 7.33 | 1.47 | 732.2 | 1.31 | 1.2 | 132.1 |
| 25[g] | **Ni-3F'** | 0 | 60 | 14.87 | 1.49 | 870.3 | 1.41 | 1.4 | 131.5 |
| 26 | **Ni-5F** | 30 | 10 | 0.56 | 0.34 | 28.0 | 1.45 | 10.8 | 115.5 |
| 27 | **Ni-5F** | 60 | 10 | 0.54 | 0.32 | 27.0 | 1.47 | 12.8 | 111.0 |
| 28 | **Ni-5F** | 90 | 10 | 0.30 | 0.18 | 16.3 | 1.82 | 17.0 | 102.6 |

[a] Reaction conditions: Ni catalyst (1 μmol), AlEt$_2$Cl (500 equiv.), toluene/CH$_2$Cl$_2$ (98 mL/2 mL), polymerization pressure (8 bar), all entries are based on at least two runs, unless noted otherwise. [b] Activity is in unit of g mol$^{-1}$ h$^{-1}$. [c] Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C or 160 °C if necessary. [d] brs = Number of branches per 1000C, as determined by $^1$H NMR spectroscopy. [e] Determined by DSC (second heating). [f] toluene/CH$_2$Cl$_2$ (148 mL/2 mL). [g] polymerization pressure (20 bar). [h] The molecular weight is beyond the GPC detector limit (1000 × 10$^4$ g mol$^{-1}$).

molecular weights compared to **Ni-0F**, although branching densities further raised to 80.2/1000 C. When installing four *para*-F atoms and eight *meta*-F atoms into **Ni-0F**, the catalyst **Ni-3F** likewise featured lower activities and lower molecular weights but higher branching densities. These results indicated that the *para*-F substituents and/or the *meta*-F substituents in α-diimine Ni(II) catalysts were slightly unfavorable for ethylene polymerization in terms of polymer molecular weights and sometimes catalytic activities; however, both could enhance branching densities of polyethylenes. We speculate that the remote electron-withdrawing fluorine substituents namely the *meta*-F substitution will reduce electron density of the α-diimine ligands, which feature a reduced coordination/stabilization towards the cationic nickel center to accelerate a deactivation, thus declining activity; even though on the other hand more electron-withdrawing ligands increase activity because ethylene insertion barriers are lower.[78] Notably, both the *para*- and/or *meta*-F substituents in α-diimine Ni(II) catalysts fail to effectively suppress the β-H elimination reaction. This should be ascribed to the absence of a C-H···F-C interaction or a Ni···F interaction (see Scheme 1).

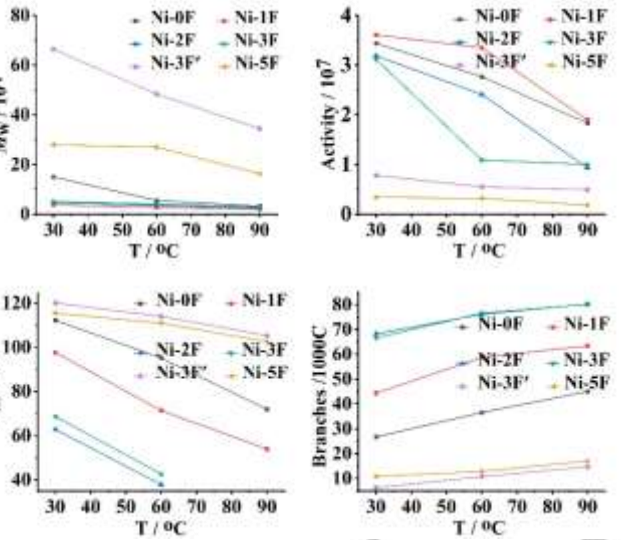


**Figure 2.** Plots of molecular weight, activity, branching density, and melting point of polyethylenes generated versus polymerization temperature with the fluorine-substituted Ni(II) catalysts **Ni-0F**~**Ni-5F** (polymerization time: 10min).

Subsequently, eight *ortho*-F atoms and four *para*-F atoms were introduced into the catalyst **Ni-0F**, and thus comprehensive studies of **Ni-3F'** were conducted to have a more insight into the role of *ortho*-F atoms in ethylene polymerization (Figure 2). Under otherwise identical conditions, compared with these catalysts **Ni-0F**~**Ni-3F** without *ortho*-F substituents, **Ni-3F'** produced polyethylenes with much higher molecular weights (up to 664 kDa at 30 °C) and far lower branching densities (6.3/1000 C at 30 °C). The polymerization results resemble those previously reported in *ortho*-F substituted nickel catalysts.[69,76] However, catalytic activities of **Ni-3F'** were significantly lower than those of **Ni-0F**~**Ni-3F**, which are similar with that by the *ortho*-F substituted cyclophane α-diimine Ni(II) catalyst,[76] but are opposite to that by the *ortho*-F substituted phenoxy-imine nickel catalyst.[69] As we know, catalytic activity depends on the rate of ethylene coordination/insertion, polymer molecular weight is determined by the rate of ethylene coordination/insertion relative to the rate of chain transfer, and branching density is dependent on the rate of chain walking relative to the rate of ethylene coordination/insertion. Based on the Guan's conclusion,[76] a proposed Ni···F interaction between the *ortho*-F substitution with the active nickel center (Scheme 1) retards the ethylene coordination/insertion, leading to the decreased activity. Decrease on activity using **Ni-3F'** probably rules out the C-H···F-C interaction that will not affect ethylene coordination. Notably, this Ni···F interaction is more pronounced to suppress the β-H elimination pathway induced by a Ni···H interaction, thus inhibiting not only chain transfer but also chain walking. As a result, polymer molecular weight increases and branching density decreases.

The pentafluorophenyl substituted catalysts such as phenoxy-imine titanium or nickel catalyst featured the best property in ethylene polymerization in terms of molecular weight,[23,69] thereby the *meta*-F atoms were further introduced into **Ni-3F'** and the per-fluorinated α-diimine Ni(II) catalyst **Ni-5F** was investigated. To our surprise, compared with **Ni-3F'** without *meta*-F atoms, catalytic activity and polyethylene molecular weight obviously declined using **Ni-5F** at all polymerization temperatures, and branching density increased slightly (Table 1, entries 14, 15 and 18 vs. 26-28). Decline on polymer molecular weight and catalytic activity should be attributed to the presence of the remote *meta*-F substituent in **Ni-5F** (relative to **Ni-3F'**), which leads to a reduced coordination/stabilization towards the cationic nickel center. Both decrease on activity and molecular weight and increase on branching density using **Ni-5F** agree with the trend using **Ni-2F**.

Since **Ni-3F'** produced remarkably higher molecular weights, more details were further studied. **Ni-3F'** showed an excellent time-dependence at 0 °C (Table 1, entries 13 and 20-23). As depicted in Figure 3a, the yield linearly increased with prolonging polymerization time from 10 to 120 minutes, which means that catalytic activity can be maintained within two hours or even a longer reaction time. Most importantly, the polymer molecular weight ($M_w$) also increased significantly to reach an amazing value of 8,216 kDa with the prolonged reaction time (Figure 3b). Notably, the polymer yield of 24.45 g corresponded to a very high turnover number (TON = $8.7 \times 10^5$), namely 14.2 kg polymer can be produced from 1 g of nickel catalyst or 414.4 kg polymer can be produced from 1 g of nickel. This polymer molecular weight was also beyond the detector limit (10,000 kDa) of the GPC instrument using in this work (Table 1, entry 23). Likewise, at higher temperature of 60 °C (Table 1, entries 15-17) the yield and the polymer molecular weight also rationally increased from 10 min, 20 min to 40 min (Figure 3c and 3d). Combined with the data at 120 °C (Table 1, entry 19), **Ni-3F'** could be acted as a thermally robust catalyst.

Increasing ethylene pressure from 8 bar to 20 bar resulted in the increase of catalytic activities and molecular weights (Table 1, entries 21 vs. 24, 22 vs. 25). The obtained polyethylene molecular weight of 8,703 kDa was extremely high, which is much higher than the value of around 5,000 kDa produced by other nickel catalysts.[8,21,48,73,78,79] Even for the classic early transition metal catalysts it is not so easy.[80] As expected, branching densities dropped at elevated ethylene pressure due to the reduced rate of chain isomerization relative to the rate of trapping of monomer. The branching distribution based on the $^{13}$C NMR analysis for the sample from Table 1, entry 24 could be referred in supporting information.

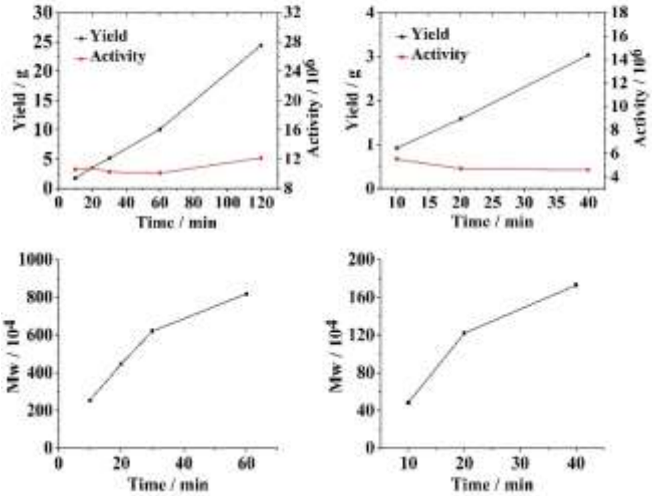


**Figure 3.** (a, Top/left) Time-dependence curves, (b, Bottom/left) Polyethylene $M_w$ as a function of time in **Ni-3F'** catalyzed ethylene polymerization, polymerization temperature: 0 °C; (c, Top/right) Time-dependence curves, (d, Bottom/right) Polyethylene $M_w$ as a function of time in **Ni-3F'** catalyzed ethylene polymerization, polymerization temperature: 60 °C.

**Mechanical properties of the obtained polyethylenes.** Generally, both polymer branching density and molecular weight are two key factors that determine mechanical properties of polymers. Therefore, a series of tensile tests of polyethylenes were carried out with different branching densities to examine themechanical properties (Figure 4). The results demonstrated that these polymer samples exhibited various strain values at break over a wide range (182%~1895%), which raised greatly with increasing branching density. Moreover, the stress values at break also displayed a wide range from 3.8 MPa to 18.3 MPa, but there was no obvious correlation between the polymer branching density and the stress value at break. Overall, the microscopic topological structure of polyethylene related to polymer physical properties can be modulated by external reaction conditions and catalyst structures.

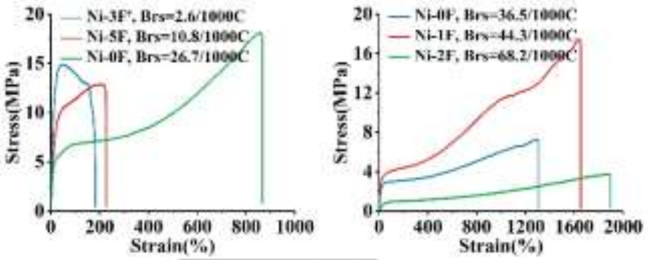


**Figure 4.** Stress−strain curves of polyethylenes with different branching densities.

**Effect of fluorine substituents on the copolymerization of ethylene and polar monomers.** In sharp contrast to studies of fluorine effect on ethylene polymerization, there is much less attention on the influence of fluorine effect on the copolymerization of ethylene and polar monomers. As the most popular polar monomers applied in α-diimine Ni(II) catalyzed olefin copolymerization,[52,56,57,62,63,65,81-85] the long-chain polar monomers including methyl 10-undecenoate (UCOOMe), 10-undecen-1-ol (UOH), 10-undecenoic acid (UCOOH), and the common monomer vinyltriethoxysilane (VTEoS) were studied in ethylene copolymerizations using the fluorinated Ni(II) catalysts. Under the activation of $AlEt_2Cl$, **Ni-3F** without *ortho*-F substituents produced the copolymer with the highest incorporation of comonomer but the lowest activity (Table 2, entry 4). **Ni-3F'** and **Ni-5F** containing *ortho*-F substituents generated notably higher molecular weight ($M_w$ up to 493 kDa) copolymers at the expense of incorporations (Table 2, entries 5 and 6). These results indicated that the presence of *ortho*-F substituent was unfavorable for the incorporation in copolymerization. Notably, copolymerization activity, molecular weight, and comonomer incorporation decreased consistently at elevated temperature of 60 °C (Table 2, entries 1 vs. 7). As anticipated, the incorporation further increased under the higher comonomer concentration at the expense of catalytic activity. It should be noted that activities of these copolymerization reactions were high relative to those using the other α-diimine nickel catalysts. Notably, **Ni-0F** was also capable of promoting copolymerization of other more challenging long-chain polar monomers. Under otherwise identical conditions, the copolymerization reactions revealed the following trends in activity: UCOOH > UOH > UCOOMe, comonomer incorporation: UCOOH > UCOOMe > UOH (Table 2, entries 8, 10, and 11). This result revealed that the acid functionalized UCOOH even behaved better than the ester functionalized UCOOMe.[86] Besides, vinyltriethoxysilane (VTEoS) was further employed in the copolymerization reaction, which gave the lowest incorporation and molecular weight compared to long-chain polar monomers, although it displayed very high activity of up to $1.47 \times 10^6$ g $mol^{-1}$ $h^{-1}$ (Table 2, entry 12).

To corroborate these copolymer microstructures, $^1$H NMR spectra and representative $^{13}$C NMR spectra, plus IR spectra were determined and analyzed as shown in Figure 5 and Supporting Information. Although the incorporation of polar monomer was relatively low, it is enough to alter the surface property of polyethylene. Incorporating 0.58 mol% of UCOOMe, 0.42 mol% of UOH, and 0.70 mol% of UCOOH into pure polyethylene decreased the water contact angles of 17.4°, 14.8°, and 20.3°, respectively (Figure 6).

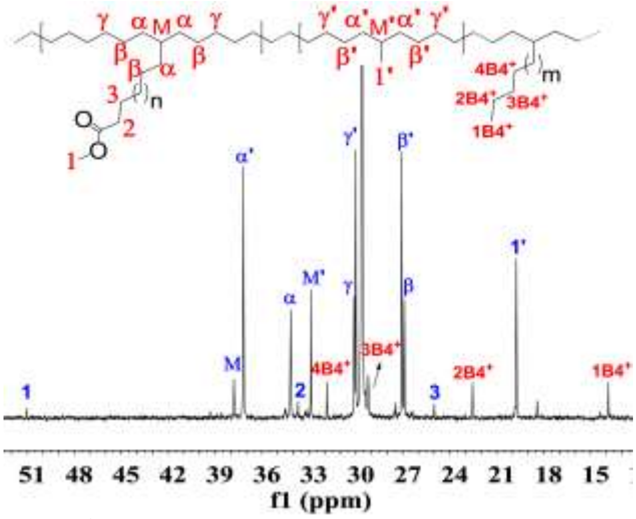


**Figure 5.** $^{13}$C NMR spectrum of the ethylene/UCOOMe copolymer (Table 2, entry 9).

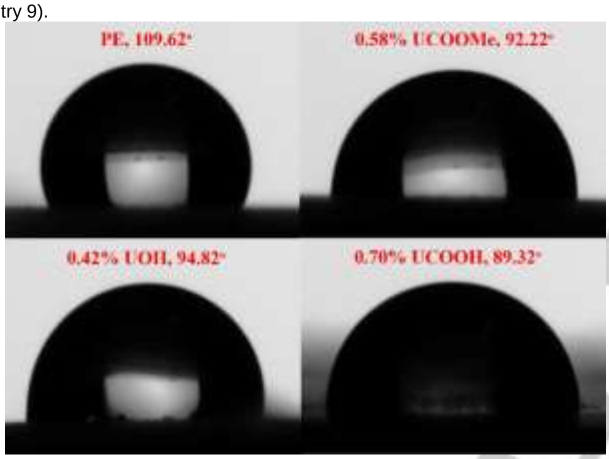


**Figure 6.** Water contact angles (WCA) of copolymers (Table 2, entries 9-11).

## Conclusions

In summary, to probe the effect of fluorine substituents in olefin polymerization catalysis, a new series of distinct fluorinated α-diimine nickel catalysts has been prepared and utilized in ethylene polymerization and copolymerization with polar monomers. In ethylene polymerization, rational conclusions can be drawn: 1) the *ortho*-F substituent is the most important, which extremely effectively suppresses the β-H elimination pathway and thus notably enhances polymer molecular weight and obviously reduces branching density of polymer; however, catalytic activity decreases probably because the proposed Ni···F interaction competes with the coordination of ethylene; 2) the *meta*-F substituent is slightly unfavorable in terms of polymer molecular weight and catalytic activity; however, branching density raises clearly. These results are entirely contrast to that in *meta*-fluorinated phenoxy-imine nickel system; 3) the *para*-F substituent mostly increases branching degree; 4) compared to the *ortho*-F substituent, the pentafluoro substituent not only reduces catalytic activity but also declines polymer molecular weight. This again verifies the negative role of the *meta*-F substituent. However, the pentafluoro substituent offers the highest polymer molecular weight in the phenoxy-imine nickel system. Moreover, in the copolymerization of ethylene with polar monomer, the *ortho*-F substituent is definitely unfavorable for the key incorporation of comonomer, and both the *meta*-F substituent and the *para*-F substituent show a slight influence in terms of incorporation. These findings indicate a unique fluorine effect in the most studied α-diimine catalysts. These insights endow a broader perspective on the fluorine effect in olefin polymerization catalysis.

**Table 2.** Copolymerization of ethylene and polar monomers with fluorinated nickel catalysts.[a]

| Entry | Cat. | Comon. | $C_{UA}$ (mol L$^{-1}$) | Yield (g) | Act. ($10^5$)[b] | $X$ (mol %)[c] | $M_w$ ($10^4$)[d] | $M_w/M_n$[d] | *brs*[c] | $T_m$[e] (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **Ni-0F** | UCOOMe | 0.05 | 4.49 | 8.98 | 0.31 | 7.1 | 2.03 | 40.0 | 101.6 |
| 2 | **Ni-1F** | UCOOMe | 0.05 | 4.97 | 9.94 | 0.25 | 5.0 | 1.88 | 46.9 | 78.8 |
| 3 | **Ni-2F** | UCOOMe | 0.05 | 2.83 | 5.66 | 0.27 | 7.0 | 1.79 | 64.1 | 53.6 |
| 4 | **Ni-3F** | UCOOMe | 0.05 | 0.74 | 1.48 | 0.35 | 8.1 | 1.74 | 58.9 | 64.4 |
| 5 | **Ni-3F'** | UCOOMe | 0.05 | 4.60 | 9.20 | 0.02 | 49.3 | 1.19 | 12.4 | 112.4 |
| 6 | **Ni-5F** | UCOOMe | 0.05 | 2.92 | 5.84 | 0.17 | 33.4 | 1.28 | 14.1 | 111.7 |
| 7[f] | **Ni-0F** | UCOOMe | 0.05 | 4.16 | 8.32 | 0.26 | 4.4 | 1.89 | 47.9 | 66.2 |
| 8[f] | **Ni-0F** | UCOOMe | 0.1 | 3.76 | 7.52 | 0.45 | 4.6 | 1.93 | 43.4 | 72.6 |
| 9[f] | **Ni-0F** | UCOOMe | 0.2 | 1.28 | 2.56 | 0.58 | 5.7 | 1.77 | 29.1 | 94.1 |
| 10[f] | **Ni-0F** | UOH | 0.1 | 4.42 | 8.84 | 0.42 | 3.8 | 2.11 | 47.4 | 77.1 |
| 11[f] | **Ni-0F** | UCOOH | 0.1 | 6.35 | 12.7 | 0.70 | 3.4 | 1.96 | 47.8 | 55.8 |
| 12[f] | **Ni-0F** | VTEoS | 0.1 | 7.35 | 14.7 | 0.10 | 2.9 | 2.02 | 51.7 | 55.7 |

[a] Reaction conditions: Ni catalyst (5 μmol), $AlEt_2Cl$ (1000 equiv.), toluene/$CH_2Cl_2$ (23 mL/2 mL), polymerization time (30 min), polymerization temperature (30 °C), polymerization pressure (4 bar), all entries are based on at least two runs, unless noted otherwise. [b] Activity is in unit of g mol$^{-1}$ h$^{-1}$. [c] $X$ = Incorporation of polar monomer, brs = Number of branches per 1000C, as determined by $^1$H NMR spectroscopy. [d] Determined by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C. [e] Determined by DSC (second heating). [f] Polymerization temperature (60 °C).

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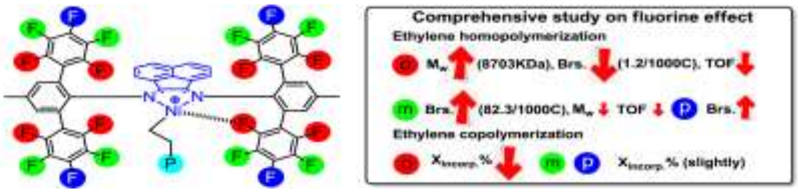

**Fluorine effect in olefin polymerization**: Fluorine substituents at various positions (ortho-, meta-, and para-) and with different numbers (n = 0, 1, 2, 3, and 5) have been systematically studied for the first time in the nickel $\alpha$-diimine promoted ethylene polymerization and copolymerization with polar monomer, which show great influence on catalytic activity, polymer molecular weight, branching density, and incorporation of polar monomer.