# Ethylene Polymerizations with Unsymmetrical (α-Diimine)nickel(II) Catalysts

By Manseong JEON and Sang Youl KIM[*]

Four unsymmetrical (α-diimine)nickel(II) catalysts were synthesized by sequential stepwise condensation of acenaphthene-quinone with the corresponding aniline compounds and subjected to ethylene polymerizations with MAO. Interestingly, when the catalysts have the same composition of the ortho substituents, the catalyst with two ortho isopropyl substitients on one side and two ortho methyl substituents on the other side produced polyethylenes with higher branching densities and lower molecular weights than the catalyst with one ortho isopropyl and one ortho methyl substituent on each side. However, branch distribution was not changed by the position of the ortho substituents.

KEY WORDS: Branched / Ethylene / Nickel / Polyethylene(PE) / Polymer Synthesis / Unsymmetrical /

Olefin polymerization catalysts based on late transition metals have attained growing interests recently, partly because of their tolerance to polar functional groups.[1–5] Especially Pd and Ni catalysts having α-diimine ligand have been of particular interest due to their easy synthesis, air stability, and novel polymerization characteristics. The catalysts activated with MAO or other cationizing reagents showed good activity for ethylene polymerizations,[6] ethylene oligomerizations,[7] α-olefin polymerizations,[8] cyclic olefin polymerizations,[9] internal olefin polymerizations,[10] copolymerizations of ethylene with protected polar functional monomers.[11,12] The catalysts have unique characteristic, production of branched polyethylene only from ethylene monomers. A chain walking (β-hydride elimination and readdition to the other carbon) followed by ethylene coordination and insertion produces a methyl branch. Repeated chain walkings followed by ethylene coordination and insertion make a longer branch.

Control of ortho substituents on aromatic rings of (α-diimine)nickel(II) catalysts is important to achieve a proper catalytic activity.[13] The ortho substituents have been reported to locate at axial site of the catalysts, and they retard chain transfer reactions, promote the chain walking, and accelerate the rate of migratory insertion. Therefore, as steric bulkiness of the ortho substituents increases, molecular weights of polyethylenes, branching densities of polyethylenes, and polymerization activities increased.[14] Some researchers further modified the ortho substituents of the (α-diimine)nickel(II) catalysts to get novel polymerization results. Brookhart et al. reported that electron withdrawing ortho substituents of the (α-diimine)-nickel(II) catalyst increased turnover frequency of ethylene polymerization presumably because electron withdrawing ortho substituents made nickel more electrophilic.[14] Rieger et al. reported chiral $C_2$ symmetric (α-diimine)nickel(II) catalysts bearing ortho phenyl substituents produced high molecular weight polyethylenes with high activities.[15] Guan et al. reported cyclophane-based (α-diimine)nickel(II) catalyst

which was highly active for ethylene polymerizations even at high temperature (~90 °C).[16] Zhu et al. reported molecular weights of the polyethylenes produced by rac-(α-diimine)-nickel(II) catalyst were significantly higher than those produced by meso-(α-diimine)nickel(II) catalyst.[17]

Another way to modify the ortho substituents of the (α-diimine)nickel(II) catalysts is making the (α-diimine)nickel(II) catalysts as unsymmetric. But there have been few reports on ethylene polymerizations with unsymmetrical (α-diimine)-nickel(II) catalysts due to the lack of proper synthetic method for unsymmetrically substituted α-diimine ligands.[18–22]

In this study, new unsymmetrical (α-diimine)nickel(II) catalysts were synthesized by stepwise acid catalyzed condensation reaction followed by condensation with $TiCl_4$/DABCO. The catalysts were subjected to ethylene polymerizations with MAO to investigate the effect of unsymmetrical ortho substituents on aromatic rings of α-diimine ligands.

## EXPERIMENTAL

Manipulations of air sensitive materials were carried out under dry nitrogen atmosphere using Schlenk flasks or a glove box.

### Materials

Toluene was refluxed over sodium and distilled under argon atmosphere. Chlorobenzene and $CH_2Cl_2$ were distilled over $CaH_2$ and stored over molecular sieves (4 angstrom). MAO purchased from Aldrich as a 10 wt.-% solution in toluene was used as received. Acenaphthenequinone, 2,6-dimethylaniline, 2-isopropyl-6-methylaniline, and nickel(II) bromide ethylene glycol dimethyl ether complex ((DME)NiBr₂) were purchased from Aldrich, and used without further purification. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was sublimed in vacuo at 40 °C. Chloroform-d was dried over molecular sieves (4 angstrom) and stored under nitrogen.

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology (KAIST), 373-1, Guseong-Dong, Yuseong-Gu, Daejeon 305-701, Korea
[*]To whom correspondence should be addressed (Tel: +82-42-869-2874, Fax: +82-42-869-8177, E-mail: kimsy@kaist.ac.kr).

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## Characterization

$^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers. Chemical shifts were recorded relative to residual CHCl$_3$ in CDCl$_3$ ($\delta$ = 7.24 for $^1$H, $\delta$ = 77.00 for $^{13}$C). Splitting patterns were designated as s (singlet), d (doublet), dd (doublets of doublet), t (triplet), dt (doublets of triplet), hep (heptet), and m (multiplet). $^1$H NMR and $^{13}$C NMR spectra of the polymers were recorded on Bruker Avance 400 spectrometers at 110 °C using tetrachloroethane-d$_2$ as a solvent. $^{13}$C NMR spectra were measured with a flip angle of 70°, an acquisition time of 1.5 s, a delay of 4.0 s, and full NOE.[23] Gel permeation chromatographic analysis were performed with Senshu Scientific High Temperature GPC (SSC-7100) equipped with two Shodex HT 806M columns and RI detector using 1,2-dichlorobenzene as an eluent at 140 °C. Universal calibration was applied using Mark-Houwink constants for polystyrene (k = $1.38 \times 10^{-4}$ and a = 0.7) and polyethylene (k = $5.6 \times 10^{-4}$ and a = 0.7).[24,25] Differential scanning calorimetry (DSC) was performed on a TA DSC Q100 connected with TA DSC Refrigerated Cooling System. The polymer was heated to 170 °C and cooled to −70 °C. After 3 min at −70 °C, second heating scan at a rate of 10 °C/min was used for the melting temperature ($T_m$) measurement of the polymer. Elemental analysis was performed on EA 1110 (CE instruments) located at Korea Basic Science Institute.

## Synthesis of ((2-Isopropyl-6-methyl phenyl)imino)-acenaphthenone (1)

Acenaphthenequinone (2.0 g, 11 mmol) and Na$_2$SO$_4$ (10 g) in 400 mL of methanol were stirred at 45 °C. 2-Isopropyl-6-methylaniline (1.6 g, 11 mmol) and formic acid (0.4 mL) in 100 mL of methanol were added dropwise to the acenaphthenequinone solution. The solution was stirred at 45 °C for 12 h. The solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (ethyl acetate:hexane = 1:4, silica gel) to afford 2.3 g of orange solid (yield = 67%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.15 (d, 2H, An $H$), 7.97 (d, 1H, An $H$), 7.79 (t, 1H, An $H$), 7.39 (t, 1H, An $H$), 7.24 (d, 1H, Ar $H$), 7.12 (m, 2H, Ar $H$), 6.66 (d, 1H, An $H$), 2.90 (hep, 1H, C$H$(CH$_3$)$_2$), 1.97 (s, 3H, C$H_3$), 1.18 (d, 3H, CH(C$H_3$)$_2$), 0.88 (d, 3H, CH(C$H_3$)$_2$).

$^{13}$C NMR (100 MHz, CDCl$_3$, selected resonances): $\delta$ = 189.55 ($C$=O), 160.26 ($C$=N), 28.40 ($C$H(CH$_3$)$_2$), 23.74 (CH($C$H$_3$)$_2$), 22.83 (CH($C$H$_3$)$_2$), 18.01 ($C$H$_3$).

C$_{22}$H$_{19}$NO: Calcd. C 84.31, H 6.11, N 4.47; Found C 84.70, H 6.24, N 4.44.

## Synthesis of ((2-Isopropyl-6-methylphenyl)imino)-((2,6-dimethylphenyl)imino)-acenaphthene (2)

2,6-Dimethylaniline (0.77 g, 6.4 mmol) and DABCO (2.2 g, 19 mmol) were dissolved in 55 mL of chlorobenzene. TiCl$_4$ (0.90 g, 4.8 mmol) in 5 mL of chlorobenzene was added to this solution dropwise at 90 °C for 30 min, followed by addition of 1 (1.0 g, 3.2 mmol) in 10 mL of chlorobenzene. The solution was stirred at 150 °C for 24 h. After cooling to room temper-

ature, the reaction mixture was filtered and the filtrate was evaporated. The product was purified by column chromatography (ethyl acetate:hexane = 1:9, including 2% triethylamine, silica gel) to afford 0.61 g of orange solid (yield = 46%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.86 (dd, 2H, An $H$), 7.35 (dt, 2H, An $H$), 7.14 (m, 6H, Ar $H$), 6.69 (t, 2H, An $H$), 3.04 (hep, 1H, C$H$(CH$_3$)$_2$), 2.13 (s, 6H, C$H_3$), 2.10 (s, 3H, C$H_3$), 1.23 (d, 3H, CH(C$H_3$)$_2$), 0.98 (d, 3H, CH(C$H_3$)$_2$).

$^{13}$C NMR (100 MHz, CDCl$_3$, selected resonances): $\delta$ = 160.94 ($C$=N), 160.77 ($C$=N), 28.65 ($C$H(CH$_3$)$_2$), 23.53, 22.69 (CH($C$H$_3$)$_2$), 17.93, 17.71 ($C$H$_3$).

C$_{30}$H$_{28}$N$_2$: Calcd. C 86.50, H 6.78, N 6.73; Found C 86.80 H 6.80, N 6.64.

## Synthesis of ((2-Isopropyl-6-methylphenyl)imino)-((2,6-dimethylphenyl)imino)-acenaphthene Nickel(II) Dibromide (3e)

(DME)NiBr$_2$ (0.13 g, 0.44 mmol), 2 (0.20 g, 0.48 mmol), and CH$_2$Cl$_2$ (12 mL) were placed in a Schlenk flask under nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated *in vacuo*. The solid was washed three times with Et$_2$O (3 mL × 3) and dried *in vacuo* to afford 0.26 g of red-brown powder (yield = 95%).

C$_{30}$H$_{28}$Br$_2$N$_2$Ni: Calcd. C 56.74, H 4.44, N 4.41; Found C 55.60, H 4.60, N 4.46.

## Ethylene Polymerization

The polymerizations were carried out in 50 mL, magnetically stirred Schlenk flasks which were thermostated at polymerization temperature and charged with toluene (total toluene: 30 mL) under nitrogen. The nitrogen atmosphere was replaced by ethylene. Under ethylene atmosphere, MAO (0.33 mL, [Al]/[Ni] = 1000) was added, and the polymerization was started by addition of a catalyst solution (0.5 µmol in 1 mL toluene). The polymerization was quenched by addition of 10 vol.% HCl/methanol solution. Polyethylene precipitated from the solution was filtered and washed with water and fresh methanol several times. The resulting polymer was dried under vacuum at 70 °C overnight.

## RESULTS AND DISCUSSION

The unsymmetrical $\alpha$-diimine ligand 2 was synthesized in two steps as shown in Scheme 1. Acid catalyzed reaction of acenaphthenequinone with 2-isopropyl-6-methylaniline gave monocondensation product 1, which was further reacted with 2,6-dimethylaniline *via* TiCl$_4$ catalyzed irreversible reaction[26–29] to obtain the unsymmetrical $\alpha$-diimine ligand 2. $^1$H and $^{13}$C NMR spectra of the unsymmetrical $\alpha$-diimine ligand 2 are shown in Figure 1. The absence of carbonyl carbon and the presence of two imine carbons in the $^{13}$C NMR spectra of 2 supported successful synthesis of 2.

Unsymmetrical ($\alpha$-diimine)nickel(II) catalyst 3e was obtained by reacting the $\alpha$-diimine ligand 2 with (DME)NiBr$_2$ in
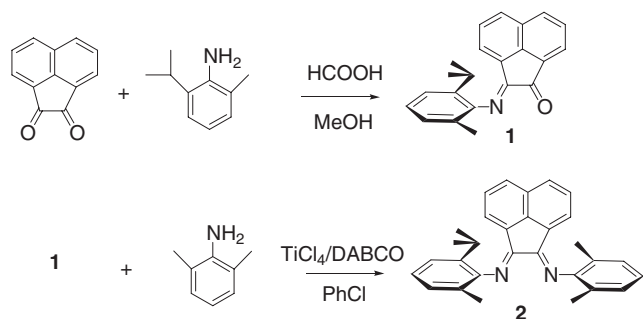
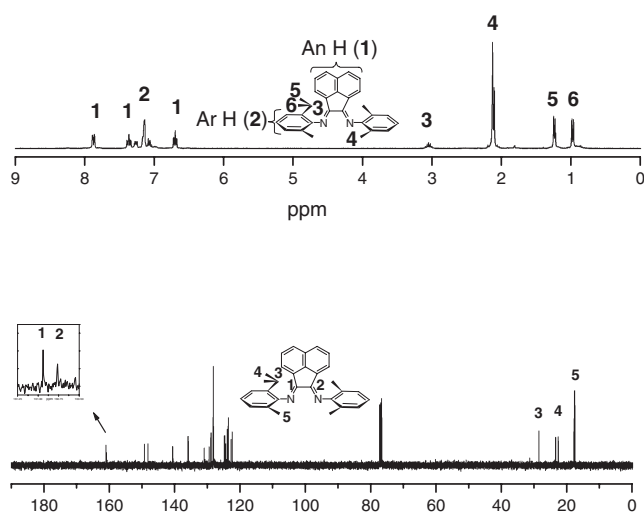**Scheme 1.** Synthesis of unsymmetrical α-diimine ligand **2**.



**Figure 1.** ¹H and¹³C NMR spectra of unsymmetrical α-diimine ligand **2**.

dichloromethane at ambient temperature. The other unsymmetrical (α-diimine)nickel(II) catalysts were synthesized according to the literatures.[21,30] The ortho substituents on aromatic rings of the unsymmetrical (α-diimine)nickel(II) catalysts are composed of isopropyl and methyl groups. The unsymmetrical (α-diimine)nickel(II) catalyst **3b** and **3e** have $C_1$ symmetry. The ortho substituents on aromatic rings of the unsymmetrical (α-diimine)nickel(II) catalysts **3c** and **3d** are

composed of two isopropyl and two methyl groups. The catalyst **3c** has $C_s$ symmetry. Two isomers of catalyst **3d**, $C_2$ symmetric form and $C_s$ symmetric form, are present, and major conformation have been reported as $C_2$.[30]

The structures of the (α-diimine)nickel(II) catalysts employed for ethylene polymerizations are summarized in Figure 2. For comparison, symmetrical (α-diimine)nickel(II) catalyst **3a** was also employed.[6] The ethylene polymerizations were carried out with the (α-diimine)nickel(II) catalysts activated by MAO in toluene at 0, 25, and 50 °C. All polymerizations were carried out with a low catalyst load (0.5 μmol) and a short polymerization time to prevent stop of stirring. Ethylene polymerization with catalyst **3d** at 25 °C was conducted with a shoter polymerization time (7.5 min). Results of the ethylene polymerizations are summarized in Table I. Catalyst **3e** showed the highest polymerization activity at 0 °C, while catalysts **3b**, **3c**, and **3d** showed the highest polymerization activities at 25 °C. Further comparison of the polymerization activity of the catalyst was stumbled, because of ethylene diffusion limit at the pressure employed in this study.[14] The polymerization activities at 50 °C were lower than those at 25 °C for all the catalysts, which attributed to the catalyst deactivation at increased polymerization temperature.[14]

Molecular weights of the polyethylenes produced with the catalysts were affected by polymerization temperature. Increases in the polymerization temperature decreased the molecular weights of the polyethylenes, which indicate the chain transfer reactions occurred more frequently at increased polymerization temperature. Each increase in the polymerization temperature by 25 °C resulted in decreases in the molecular weights of the polyethylenes by almost half.

The polymerization temperature affected branching densities and melting temperatures of the polyethylenes. Increases in the polymerization temperature resulted in the increased branching densities of polyethylenes and the decreased melting temperatures of polyethylenes, which stem from the enhanced chain walking relative to the ethylene coordination and insertion at increased polymerization temperature.[14]

The polymerizations at 50 °C were more homogeneous than the polymerizations at 0 °C or 25 °C because the polyethylenes
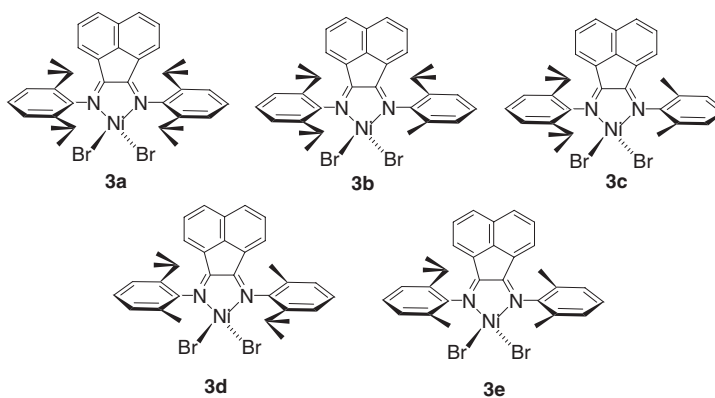


**Figure 2.** (α-Diimine)nickel(II) catalysts employed for ethylene polymerizations.

**Table I.** Ethylene Polymerization Results[a]

| Run | Catalyst | $T_p$[b] (°C) | Yield (mg) | Activity (kg of PE/mol of catalyst·atm·h) | $M_n$ | PDI | Branches per 1000 carbons[c] | $T_m$ (°C)[d] |
|-----|----------|-----------|-----------|---------|-------|------|----------|----------|
| 1 | **3a** | 50 | 347 | 2220 | 69000 | 2.12 | 113 | −27 |
| 2 | **3b** | 0 | 336 | 2150 | 310000 | 2.98 | 7 | 120 |
| 3 | **3b** | 25 | 481 | 3080 | 104000 | 2.22 | 55 | 63 |
| 4 | **3b** | 50 | 306 | 1960 | 35000 | 1.99 | 95 | −8 |
| 5 | **3c** | 0 | 413 | 2640 | 256000 | 3.26 | 9 | 122 |
| 6 | **3c** | 25 | 616 | 3940 | 66000 | 2.00 | 52 | 69 |
| 7 | **3c** | 50 | 372 | 2380 | 24000 | 2.00 | 89 | 16 |
| 8 | **3d** | 0 | 283 | 1810 | 211000 | 3.01 | 2 | 125 |
| 9[e] | **3d** | 25 | 520 | 6656 | 79000 | 3.74 | 36 | 85 |
| 10 | **3d** | 50 | 397 | 2540 | 30000 | 1.72 | 83 | 29 |
| 11 | **3e** | 0 | 939 | 6010 | 179000 | 3.58 | 10 | 120 |
| 12 | **3e** | 25 | 699 | 4370 | 60000 | 3.19 | 29 | 94 |
| 13 | **3e** | 50 | 382 | 2440 | 13000 | 1.79 | 76 | 15, 43 |

a) Polymerization condition: total toluene = 30 mL, ethylene pressure = 1.25 atm, polymerization time = 15 min (except run 9), (α-diimine)nickel(II) catalysts = 0.5 μmol, [Al]/[Ni] = 1000. b) Polymerization temperature. c) Calculated by ^{1}H NMR. d) Determined by DSC. e) Polymerization time = 7.5 min.

produced at 50 °C were branched polymers with low molecular weights. So the polyethylenes produced from the polymerizations at 50 °C showed narrower PDI (∼2.0) than those produced from the polymerizations at 0 °C or 25 °C. The polyethylene produced by catalyst **3d** at 25 °C showed highest PDI among the catalysts employed at the samepolymerization temperature, presumably due to the presence of two isomers of catalyst **3d**, $C_2$ symmetric form and $C_s$ symmetric form.[17]

Molecular weights of the polyethylenes produced with the catalysts were also affected by the catalyst structure. Decrease in steric bulkiness of the ortho substituents on aromatic rings of the (α-diimine)nickel(II) catalysts decreased the molecular weights of the polyethylenes, because sterically less bulky ortho substituents enhance the chain transfer. Polymerizations at 50 °C showed this tendency clearly (compare run 1 with 4, 7, 10, and 13). It is interesting to compare catalyst **3c** with **3d**, because their ortho substituents are same but are located at different positions. While catalyst **3c** contains two ortho isopropyl substitients on one aromatic ring and two ortho methyl substituents on the other aromatic ring, catalyst **3d** contains one ortho isopropyl and one ortho methyl substituent on each aromatic ring. For the polymerization at 25 °C, catalyst **3c** produced polyethylene with lower molecular weight ($M_n = 66000$) than that ($M_n = 79000$) obtained by catalyst **3d**. For the polymerization at 50 °C, the molecular weight of the polyethylene produced with **3c** was also lower than that of the polyethylene produced with **3d** ($M_n = 24000$ for **3c** and $M_n = 30000$ for **3d**). It seems that the rate of chain transfer relative to ethylene coordination and insertion for catalyst **3c** is higher than that for catalyst **3d**.[17] It was difficult to observe the effect of catalyst structure on the molecular weights of the polyethylenes obtained at 0 °C, because of the premature precipitation of the polyethylenes.

Decreased steric bulkiness of the ortho substituents on aromatic rings of the (α-diimine)nickel(II) catalysts decreased branching densities of the polyethylenes and increased melting temperatures of the polyethylenes, because sterically less bulky ortho substituents enhance the axial approach of ethylene, resulting in a reduced chain walking relative to the ethylene coordination and insertion. The effect was evident for ethylene polymerizations at 50 °C. Decrease in the number of ortho isopropyl substituents resulted in decreased branching densities of the polyethylenes and increased melting temperatures of the polyethylenes. Interestingly, catalyst **3c** afforded polyethylenes with higher branching densities and lower melting temperatures than the polyethylene produced by catalyst **3d**, which indicates that the rate of chain walking relative to the ethylene coordination and insertion for catalyst **3c** is higher than that for catalyst **3d** (compare run 5 with 8, 6 with 9, and 7 with 10). When the polymerizations were carried out at 0 °C, the catalysts afforded polyethylenes with few branches per 1000 carbons.

Branch distributions of the representative samples were analyzed by ^{13}C NMR, and the results are shown in Table II.[23,31] Methyl branch was a dominant branch, while ethyl, propyl, butyl, amyl, and long branch were minor branches. The order of branch was methyl ≫ long > ethyl > propyl ∼ butyl > amyl, which was similar to the previous result.[23] Increased polymerization temperature decreased percentage of methyl branch and increased percentage of the other branches, because of enhanced chain walking relative to ethylene coordination and insertion. The two catalysts, **3c** and **3d**, resulted in the same branch distributions with dominant methyl branch.

**Table II.** Branch Distributions of Representative Polyethylenes[a]

| Run | Methyl | Ethyl | Propyl | Butyl | Amyl | Long | Total |
|-----|--------|-------|--------|-------|------|------|-------|
| 6 | 35 (67.6) | 4 (7.9) | 3 (5.8) | 3 (5.2) | 2 (3.0) | 5 (10.5) | 52 (100.0%) |
| 7 | 56 (62.7) | 9 (9.6) | 5 (5.9) | 5 (6.1) | 3 (3.1) | 11 (12.6) | 89 (100.0%) |
| 10 | 53 (63.9) | 7 (8.4) | 5 (6.0) | 5 (6.3) | 3 (3.7) | 10 (11.7) | 83 (100.0%) |

a) The number in the bracket denotes branch percentage.

## CONCLUSION

Ethylene polymerizations with the unsymmetrical (α-diimine)nickel(II) catalysts produced branched polyethylenes. As the polymerization temperature increased, the molecular weights of the polyethylenes decreased and the branching densities of the polyethylenes increased. Decreases in the steric bulkiness of the ortho substituents resulted in the decreased molecular weights of the polyethylenes and the decreased branching densities of the polyethylenes. When the catalysts have the same composition of the ortho substituents, the catalyst with two ortho isopropyl substitients on one side and two ortho methyl substituents on the other side (**3c**, $C_s$ symmetry) produced polyethylenes with higher branching densities and lower molecular weights than the catalyst with one ortho isopropyl and one ortho methyl substituent on each side (**3d**, $C_2$ symmetry), presumably because the rate of chain walking and chain transfer for the catalyst **3c** is higher than the catalyst **3d**. The position of the ortho substituents did not affect the branch distributions of the polyethylenes.

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